Part I Optimization of Palladium Catalyzed Phosphination

Part II Syntheses of Optically Active As,N Ligands and Their Metal Complexes

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于子洋

A Thesis Submitted in Partial Fulfillment

of the Requirements for the Degree of

Master of Philosophy

in

Chemistry

To My Supervisor

Professor

Kin Shing Chan


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July 2003

Michael Yu

Department of Chemistry

The Chinese University of Hong Kong

Abbreviations

δ	: chemical shift	m	: multiplet (NMR)
^{n}Bu	: *n*-butyl	M^{+}	: molecular ion
^{t}Bu	: *t*-buthy	*m/z*	: mass per charge ratio
Calcd.	: calculated	Me	:methyl
Cy	: cyclohexyl	mg	: milligram(s)
d	: day(s)	min	: minute(s)
d	: doublet (NMR)	mL	: milliliter(s)
dba	: (*E,E*)-dibenzylidieneacetone	mmol	: millimole(s)
dd	: double doublets	MHz	:megahertz
DME	: dimethoxyethane	MS	: mass spectrometry
DMF	: dimethylformamide	Np	: naphthyl
DMSO	: dimethylsulfoxide	NMP	: *N*-methylpyrrolidinone
dppe	: diphenylphosphinoethane	NMR	: nuclear magnetic resonance
dppp	: diphenylphosphinopropane	Py	: pyridine
EI	: electron impact (MS)	q	: quartet (NMR)
Et	: ethyl	Rt	: room temperature
FG	: functional group(s)	s	: singlet
GC	: gas chromatography	t	: triplet (NMR)
g	: gram(s)	THF	: tetrahydrofuran
h	: hour(s)	Tf	: trifluoromethylsulfonyl
J	: coupling constant	TLC	: thin layer chromatography

Abstract of thesis entitled:

Part I **Optimization of Palladium Catalyzed Phosphination**

Part II **Syntheses of Optically Active As,N Ligands And Their Metal Complexes**

Submitted by Michael Yu

For the degree of Master of Philosophy

at The Chinese University of Hong Kong in July 2003

Part I

The user-friendly palladium catalyzed phosphination of aryl bromides using triarylphosphines as the phosphinating reagents was successfully optimized by the addition of iodides. The added iodides enhanced both the yields and the rates of reactions.

Part II

Novel optically active As,N-oxazolines were synthesized. Palladium and platinum complexes were successfully synthesized. The palladium complexes of *iso*-propyl and benzyl substituted As,N-oxazolines were further characterized by single crystal X-ray crystallography.

摘要

Ⅰ 鈀催化膦化反應的優化

Ⅱ 砷氮類呃唑啉及其絡合物的合成

Ⅰ

以三芳基膦爲膦化劑，通過加入碘鹽，鈀催化的芳基溴化物膦化反應被成功優化。加入碘鹽後，反應產率和速度均得到提高。

Ⅱ

新的光活性砷氮類呃唑啉被成功合成。其鈀和鉑的絡合物也被成功製備。通過 X 光單晶衍射，異丙基和苄基取代的砷氮類呃唑啉鈀絡合物結構得到進一步確認。

Part I - Optimization of Palladium Catalyzed Phosphination

Chapter 1 General Introduction

1.1 Background of Phosphine Synthesis

As with much organic chemistry, organophosphorus chemistry began in the nineteenth century. The pioneers of organophosphorus chemistry are P. E. Thenard and especially A.W. von Hofmann who worked in the laboratory of Karl Arnold August Michaelis at the University of Rostock in Germany from 1874 to 1916 leading the characterization and discovery of some of the major functional groups and their synthetic methods that we still use today.[1] Every year onwards, a large number of methods in preparation of phosphines are reported, most of them are useful improvements and extensions to some methods. However, there had been no significant addition of synthetic methods of phosphines to the list given by Maier which was published in 1972.[2,3] In the list, there are three general synthetic methods which are used for the preparation of the majority of phosphorus-carbon and phosphorus-hydrogen bonds by:

i) Organometallic reagents and halogenophosphines

ii) Metal phosphides

iii) Transition metal catalyzed phosphination

The source of the phosphorus atom in the preparation of organophosphorus compounds is mostly elemental phosphorus and in other words, the lowest numbers of synthetic steps from it gives the most efficient and effective method. Unfortunately, useful synthesis of phosphines directly from elemental phosphorus is limited in scope. Therefore, most syntheses make use of commercially available derivatives like halogenophosphines. It is important to improve the phosphines and to synthesize new organophosphorus compounds since phosphines, by their lone pair electrons, can act as ligands for metal catalyzed reactions. The steric and electronic effect of phosphines can be altered by changing the substituient and therefore, the effectiveness of ligands.

The steric bulk of a phosphine can be measured by the cone angle (θ). As defined by Tolman,[4] cone angle is the plane angle at the apex of a cone located at the center of the central metal atom of the complex and where the surface of the cone compasses the ligand, passing at a distance from the outermost atoms of the ligand equal to the effective van der Waals radii of those atoms. The steric bulk increases with increasing cone angle as shown in Figure 1.1. The electronic effect of a phosphine can be measured by its p*K*a[1] (Table 1.1). The electron donating ability of a phosphine increases with increasing basicity or equivalently p*K*a.

Figure 1.1 Cone angle

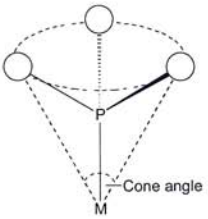


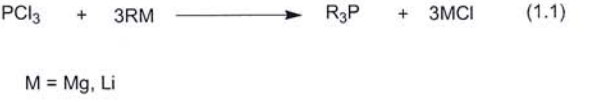
Table 1.1 Stereoelectronic Properties of Phosphorus(III) Ligands[15]

No.	Ligands	Cone Angle /^{O}C	p*Ka*
1	$P(OMe)_3$	107	2.6
2	$P(OMe)_2Ph$	120	2.64
3	$P(OPh)_3$	128	-2.00
4	$P(OMe)Ph_2$	132	2.69
5	PBu_3	132	8.43
6	$PMePh_2$	136	4.57
7	$PEtPh_2$	140	4.9
8	P(*O*-o-tol)$_3$	141	-1.83
9	PPh_3	145	2.73
10	P(*p*-MeOPh)$_3$	145	4.59
11	$PCyPh_2$	153	5.05
12	PCy_3	170	9.7
13	P(*t*-Bu)$_3$	182	11.4

1.2 Preparation of Phosphines

Preparation via Electrophilic Phosphorus And Organometallic Reagents

Organophosphines are synthesized from the reactions of electrophilic phosphorus and organometallic reagents.

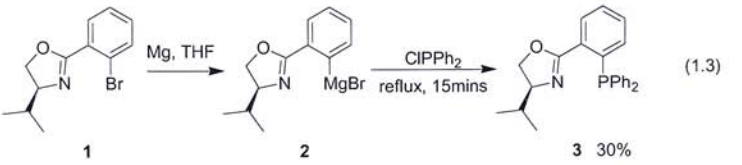


Equation 1.1 illustrates the general chemical transformation. This method is often firstly considered due to the readily available halogenophosphines. However, the halogenophosphines are very air and moisture sensitive as well as toxic, making them difficult to handle in laboratory. This method is useful in the preparation of tertiary phosphines but not in the synthesis of primary and secondary phosphines since halophosphines of H_2PCl and $HPCl_2$ are not commercially available. Moreover, this method is limited to base insensitive compounds only.

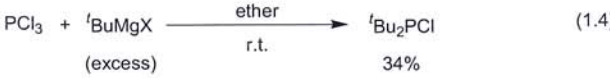
Use of Grignard Reagents

Phosphination via Grignard reagents are often employed (Equation 1.2). One

unique example is shown in Equation 1.3 for the preparation of oxazoline phosphine.[5]



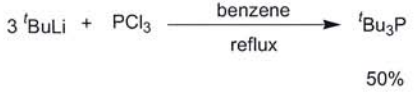
This organometallic approach generally suffers from poor yield if the anion is sterically hindered. The reaction of 2-oxazolinyl phenyl magnesium bromide **(2)** only yields the corresponding phosphine in 30% (Equation 1.3). ^{t}BuMgBr, even in excess, only produces the di-^{t}butyl but not the tri-^{t}butyl phosphine (Equation 1.4).[6]



Use of Organolithium Compounds

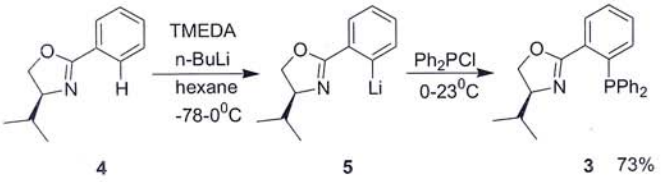
Li-C bonds are generally more ionic than Mg-C bond,[7] organolithiums are

therefore more reactive than Grignard reagents. Indeed the sterically hindered tri-^{t}butylphosphine can be obtained from the reaction of ^{t}BuLi and PCl_3 in 50 % yield (Equation 1.5)[8] where ^{t}BuMgBr fails to give any desired product.



(1.5)

Likewise, the 2-oxazolinylphenyl lithium, generated from orthometalation of sterically hindered 2-phenyloxazoline with butyl-lithium and TMEDA in hexane, reacts with Ph_2PCl to give a higher yield of the product than 2-oxazolinylphenyl magnesium bromide (Equation 1.6).[9]



(1.6)

Preparation via Nucleophilic Phosphorus From Metal Phosphide

Althernatively, phosphines can be prepared from nucleophilic phosphorus reagent. Primary and secondary phosphines are metallated by strong base of sodium or potassium in liquid ammonia and butyllithium (Equations 1.7-1.10).[2]

$$PH_3 + KNH_2 \longrightarrow KPH_2 + NH_3 \quad (1.7)$$

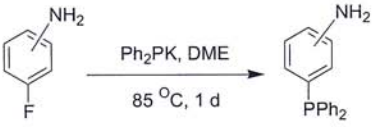
$$Ph_2PH + NaNH_2 \longrightarrow Ph_2PNa + NH_3 \quad (1.8)$$

$$Ph_2PCl + LiBu \longrightarrow Ph_2PLi + BuCl \quad (1.9)$$

$$Ph_2PH + LiBu \longrightarrow Ph_2PLi + BuH \quad (1.10)$$

Table 1.2 shows the results of the syntheses of *ortho*, *meta* and *para* isomers of diphenylphosphinobenzylamines from $Ph_2P^-K^+$ and fluorobenzylamines.[10] Likewise, by using diphenylphosphane in superbasic conditions with DMSO as solvent, diphenylphosphinobenzonitrile can be synthesized in good yields.[10] The *para* isomer gives better yield than those of *ortho* and *meta* substituted benzonitrile suggesting that the reaction is sensitive to steric hindrance (Table 1.3).

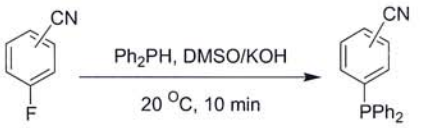
Table 1.2. Synthesis of diphenylphosphinobenzylamine



(1.11)

Isomer	Yield /%
Ortho	95
Meta	56
Para	70

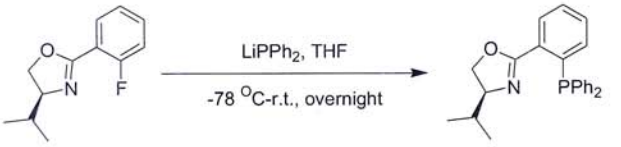
Table 1.3 Synthesis of diphenylphosphinobenzonitrile



(1.12)

Isomer	Yield /%
Ortho	82
Meta	82
Para	92

The oxazoline phosphine is also prepared in good yields from the Ph_2PLi and 2-oxazolinyl phenyl fluoride **(6)** (Equation 1.13).[5]



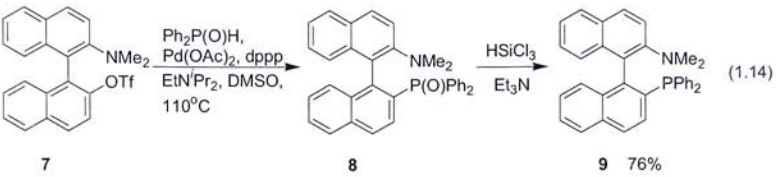
(1.13)

6 **3** 67%

Transition Metal Catalyzed Phosphination

The previously mentioned traditional methods of phosphine syntheses often employ very basic reagents. Recently, milder phosphination methods by transition metal catalyzed phosphination reactions have been developed. One example is the palladium-catalyzed phosphinylation of the biaryl triflate using air and moisture

stable diphenylphosphine oxide as the phosphinylating reagent (Equation 1.14).[11]



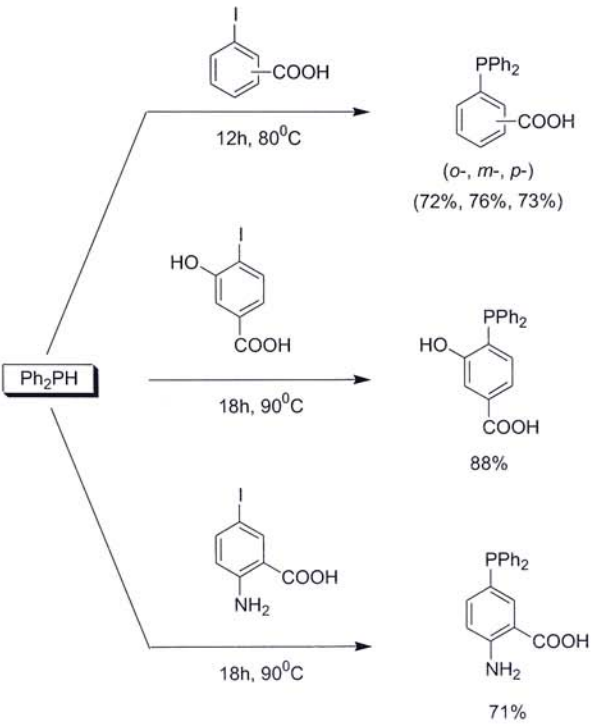
(1.14)

7 8 9 76%

However, subsequent reduction of phosphine oxide is required. Therefore substrates bearing easily reducible functional groups are not compatible. Reductants such as lithium aluminium hydride, sodium borohydride, triphenyl phosphite, etc can also be used.[12] So far, the most commonly employed reducing reagent is trichlorosilane because of its broader scope and mildness.[13]

In 1998, palladium-catalyzed P-C coupling reactions between primary or secondary phosphines and functionalized iodoarenes was developed by Herd and co-workers.[14] This coupling reaction eliminates the reduction step and tolerates substituents like OH, NH_2 and COOH (Scheme 1.1). However, this C-P coupling reaction uses expensive, air and moisture sensitive primary and secondary phosphines. Moreover, it is limited to aryl iodides.

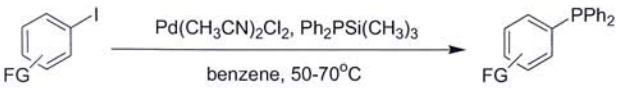
Scheme 1.1 Pd catalyzed P-C coupling reactions with Ph_2PH



Conditions: $Pd(OAc)_2$, NEt_3, CH_3CN

Another phosphinating reagent, (trimethylsilyl)diphenylphosphine, has also been developed in palladium-catalyzed phosphination reaction.[15] It does not need further reduction and the phosphinating reagent is fairly air stable (Equation 1.15). This phosphination reaction is compatible with various of functional groups such as ketone, methyl ether and halides. However, hydroxyl, amino, nitro and aldehyde groups are not tolerated. Moreover, this reaction is limited to aryl

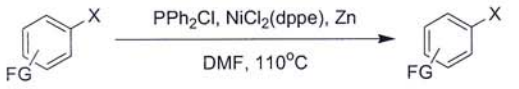
iodides and Ph_2PSiMe_3 is moisture sensitive and not commercially available.



(1.15)

FG = $COCH_3$, $COOCH_3$, Br, Cl, CF_3, OCH_3

Instead of palladium, nickel complexes are also active phosphination catalysts.[16] Air and moisture sensitive chlorodiphenylphosphine is used as the phosphinating reagent in phosphination catalyzed by $NiCl_2$(dppe), together with zinc metal functioning as the reducing agent to convert nickel(II) to nickel(0) and provide Ph_2PZnCl for transmetallation (Equation 1.16). This method tolerates functional groups such as methoxy, methyl ether, amine and amide but not carboxylic acid and easily reducible functional groups since zinc metal is used.



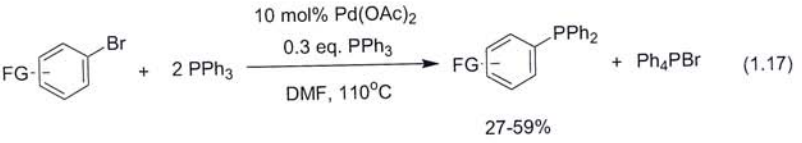
(1.16)

X = Br, OTf

FG = $COOCH_3$, OCH_3, NHBn

Recently, a novel palladium catalyzed phosphination methodology of aryl triflates and bromides using economical triarylphosphines as the diaryl

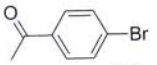
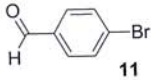
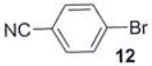
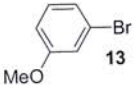
phosphinating reagents and $Pd(OAc)_2$ catalyst has been developed in Chan's group (Equation 1.17).[17,18,19] This method is compatible with many functional groups such as ketone, aldehyde, nitrile and methoxy groups (Table 1.4).[18]



(1.17)

FG = aldehyde, chloride, cyano, ester, methyl ether and ketone

Table 1.4 Palladium catalyzed phosphination of aryl bromides

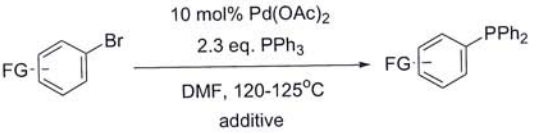
Substrate	Time /h	Yield /%
 **10**	20	40
 **11**	64	32
 **12**	48	36
 **13**	18	38

Protection/deprotection steps in traditional phosphination methodology are

not required. Triarylphosphines are relatively inexpensive and readily available. Moreover, triarylphosphines are air and moisture stable. Thus, syntheses of substituted aryl phosphines are operationally simple, user-friendly and economically attractive.[20] However, the reaction rate and yield are not very satisfactory.

1.3 The Objective of This Work

Since phosphine derivatives are very important in fine-tuning the efficiency and effectiveness of transition metal catalysis. The previous synthetic methods of phosphines are limited in scopes.[9-16] The method developed by Chan and et. al. suffers from low yielding and requirement of high reaction temperature, further improvement is necessary. This part of the thesis concerns the enhancement on reaction rate and yield in palladium-catalyzed phosphination of aryl bromides by the addition of additives (Equation 1.18).

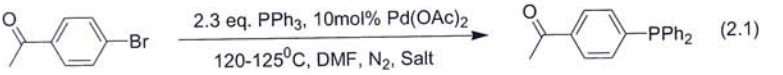


(1.18)

Chapter 2 Optimization of Phosphination of Aryl Bromides

2.1 Additive effect in phosphination reaction

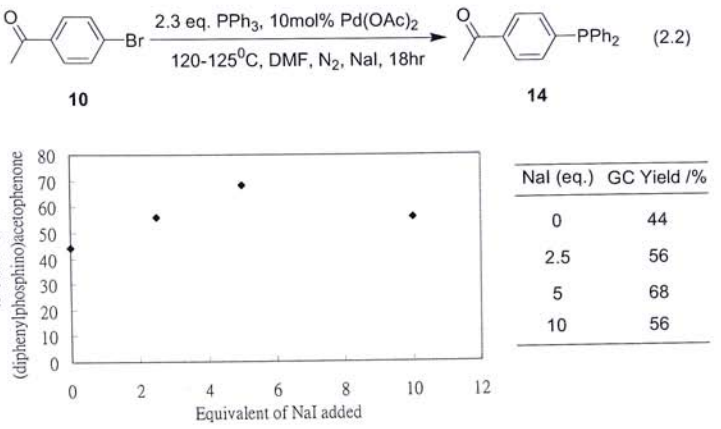
It is known that in some palladium-catalyzed reactions, metal halides such as sodium iodide[21] and copper iodide[22] can enhance the reaction rate and yield dramatically. Optimization of the novel palladium-catalyzed phosphination was therefore carried out using sodium iodide in the phosphination of 4-bromoacetophenone as a prototype substrate (Equation 2.1).



10 **14** (2.1)

The reactions were monitored by GC-MS using anthracene as the internal standard. In order to investigate the optimal loading of additive, 2.5, 5 and 10 equivalents of NaI were added. The results are shown in Table 2.1.

Table 2.1 Effect of NaI loading on phosphination of 4-bromoacetophenone

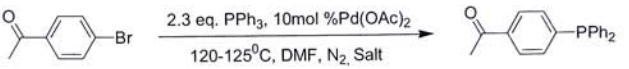


NaI (eq.)	GC Yield /%
0	44
2.5	56
5	68
10	56

*GC yield

Sodium iodide was found to increase the yield of phospination reaction of 4-bromoacetophenone using 10 mol% of $Pd(OAc)_2$ and 2.3 equivalents of PPh_3 in DMF at 120-125°C in 18 hours. The optimum loading of sodium iodide was estimated to be about 5 equivalents and a good yield of 68 % of the product was obtained. Higher loading of 10 equivalents of NaI, however decreased the yield. In all cases, no rate enhancement was observed. With these successful results obtained, further additives were examined and the results are listed in Table 2.2.

Table 2.2 Different Salts in Phosphination of 4-Bromoacetophenone by $Pd(OAc)_2$



14

Entry	Salt (5eq.)	Time/hr[a]	GC Yield/%
1	—	20	46[b]
2	**NaI**	**20**	**68**
3	**NaBr**	**23**	**65**
4	NaCl	23	51
5	$NaNO_3$	20	38
6	$NaBF_4$	22	34
7	NaOAc	23	0
8	$NaPF_6$	20	0
9	**KI**	**10**	**67**
10	KBr	10	40
11	KF	10	8
12	K_3PO_4	20	0
13	CsCl	20	45
14	CsF	20	0
15	**Et_4NI**	**2**	**49**
16	NH_4PF_6	26	0
17	**LiI**	**6**	**51**
18	CuI	10	2
19	$BF_3.Et_2O$	12	17
20	0.1eq.Cy_3P	15	40
21	0.2eq.Cy_3P	40	49

a) Complete disappearance of starting material and optimal amount of product.
b) Isolated yield.

Among the additives, halides gave better yields of product and enhanced the rates of reactions (Table 2.2, entry 2-4, 9-10, 17). Among the halides, sodium and potassium halides exhibited similar promoting effect. Iodides (MI, M = Li, Na, K) were most superior. They enhanced faster reaction and higher yields of the product (Table 2.2, entry 2-5, 9-10, 15, 17). The time profiles of different salts in the reaction are shown in Graph 2.3.

Graph 2.3 Time Profile of Different Iodides In Phosphinaiton of 4-Bromoacetophenone

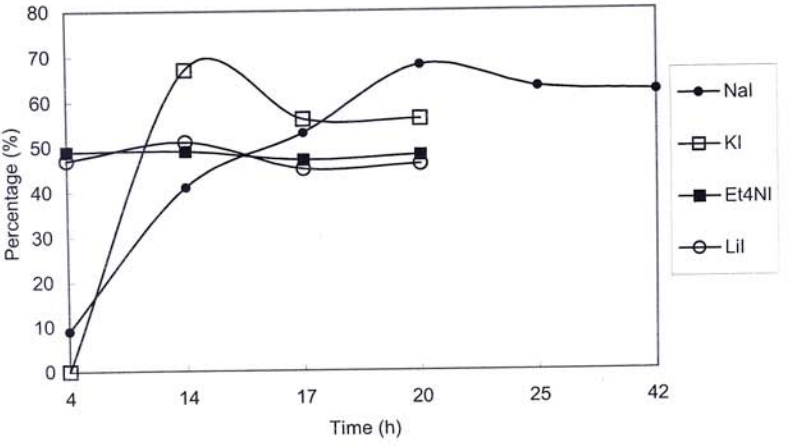


Table 2.3a

Time (h)	NaI (Yield/%)
4	9
14	41
17	53
20	68
25	63
42	62

Table 2.3 b

Time (h)	KI (Yield/%)
2	0
10	67
20	56
22	56

Table 2.3c

Time (h)	Et_4NI (Yield/%)
2	49
7	49
16	47
20	48

Table 2.3d

Time (h)	LiI (Yield/%)
2	47
6	51
10	45
20	46

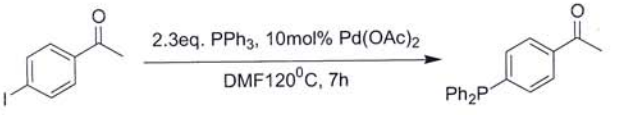
GC Yield was reported.

Sodium iodide increased the yield from 46 % (Table 2.2, entry 1) to 68 % (Table 2.2, entry 2). Potassium iodide not only increased the yield of phosphination reaction to 67 % but also shortened the reaction time from 20 to 10 hours (Table 2.2, entry 9). Although tetraethylammonium iodide (Table 2.2, entry 15) did not increase the yield of phosphination, however, it shortened the phosphination reaction time from 20 hours to 2 hours (Table 2.2, entry 1).

Alkali metal iodide generally showed better yields of the phosphination reaction. The best result was found to be with the addition of 5 equivalents of KI,

with the isolated yield of 4-(diphenylphosphino)acetophenone obtained in 60% in 10 hours. Non-halide salts such as, $NaBF_4$, $NaPF_6$ and NH_4PF_6 were found to inferior both in rates and yields.

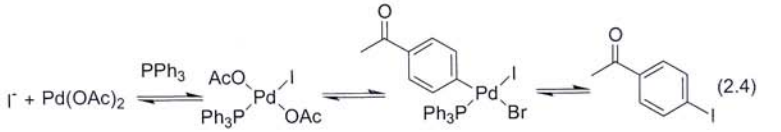
The metal halides likely play several roles in the phosphination reaction. The addition of metal halides may increase the polarity of the solvent that favors the oxidative addition and the formation of the phosphonium salt intermediate. The iodide may further assist the halide exchange of an aryl bromide to a more reactive aryl iodide.[23] The possibility of converting aryl bromide to aryl iodide by the addition of NaI or KI was supported by the observation of a trace amount (~2%) of 4-iodoacetophenone generated during the reaction of phosphination of 4-bromoacetophenone detected by GC-MS analysis (Scheme 2.1). Likely, this is formed by the reductive elimination of an Ar-Pd-I intermediate. 4-Iodoacetophenone **(15)** indeed was found to react about 3 times faster than 4-bromoacetophenone in the phosphination (Equation 2.3).



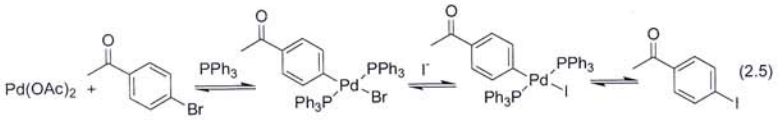
(2.3)

15 **14** 44%

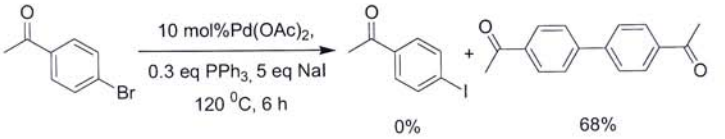
There are two possible ways to form 4-iodoacetophenone. The first one was that the iodide anion coordinates with $Pd(OAc)_2$ to form an active catalyst $Pd(OAc)_2I(PPh_3)$. Further reduction by PPh_3 and oxidative addition of 4-bromoacetophenone generates an intermediate $PdBrI(Ar)(PPh_3)$. After reductive elimination, 4-iodoacetophenone was formed (Equation 2.4).



The second way is that the $Pd(OAc)_2$, after reduction by PPh_3, undergoes oxidative addition of 4-bromoacetophenone. Then the iodide anion exchanged with the bromide in the resultant intermediate. 4-Iodoacetophenone finally is generated by reductive elimination (Equation 2.5).

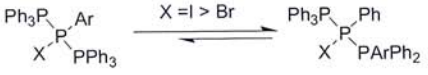


However, aryl bromide did not undergo exchange with iodide (Equation 2.6). The major product was found to be the coupled biaryl in 68% yield. Therefore, 4-iodoacetophenone might have been formed in a minor pathway in phosphination reactions or under high phosphine concentration.



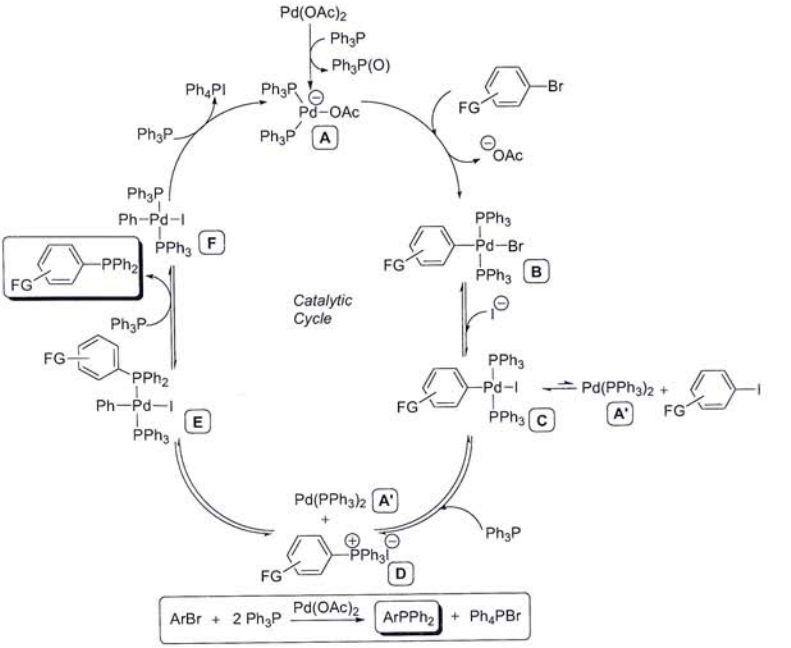
(2.6)

Less coordinating anions were reported to have faster dissociation (BF_4^-> I^-> Br^-> Cl^-).[24] Since iodide anion is less coordinating, therefore it dissociates more rapidly than bromides and chlorides, and the concentration of coordinatively unsaturated palladium species would increase. The rate of Pd-aryl/P-aryl exchange is therefore faster (Equation 2.7). Such anion dependent exchange has been reported by Grushin.[25]



(2.7)

Scheme 2.1 A Plausible Mechanism for Palladium-Catalyzed Phosphination with Added Iodides.

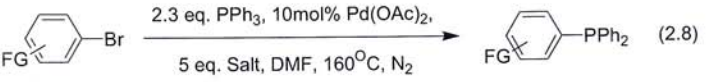


Scheme 2.3 illustrates a plausible mechanism for the reaction involving Pd(0)/Pd(II) cycles. Palladium(II) acetate is *in situ* reduced by triphenylphosphine to form acetate ligated complex **A,** $PdL_2(OAc)^-$ (L = triphenylphosphine).[26,27] This active anionic palladium complex **A** then undergoes oxidative addition with an aryl bromide to afford four-coordinated palladium complex **B** (Scheme 2.1).[28] Halide exchange by the addition of iodide ion (from NaI or KI) generated complexes **C**. As a trace and real amount of 4-iodoacetophenone was observed during the course of the reaction by GC-MS analysis,[29] the ligand substitution product from **B** to **C** is

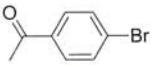
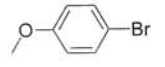
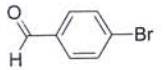
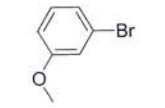
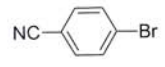
feasible. The *trans*-complex **C** subsequently, after isomerization to the cis-isomer, undergoes reductive elimination with triphenylphosphine to produce a phosphonium salt **D** and palladium complex **A'**. Such Pd-catalyzed phosphonium salt formation for *meta*- and *para*- but not *ortho*-substituted aryl bromides has been reported.[30] Grushin *et al.* also reported that the palladium iodide complex undergoes the Pd-aryl/P-aryl interchange faster than bromide and chloride[24] through possibly the phosphonium salt pathway in the $ArPdX(PPh_3)_2$ complex.[25] The anionic palladium complex **A** then undergoes oxidative addition by carbon-phosphorus bond activation of the phosphonium salt **D** to generate the coordinated $ArPPh_2$ Pd-complex (Scheme 2.1).[31,32] Finally, ligand substitution by triphenylphosphine to Pd(II) complex **E** gives $ArPPh_2$ and Pd-phenyl complex **F**. The $PdL_2(OAc)^-/PdL_2I^-$ species is regenerated by reductive elimination of triphenylphosphine and Pd bound phenyl group to yield the tetraphenylphosphonium iodide co-product (Scheme 2.1). The formation of tetraphenylphosphonium co-product was detected by ^{31}P NMR (δ = 24.0 ppm)[33] in the reaction mixture. Therefore, two equivalents of PPh_3 were required. The first one serves as the diphenylphosphinating agent and the second one yields the phosphonium salt co-product.

The iodide enhancement effect in phosphination was found to be general in aryl bromides. With the rates increased nearly about two times and yields increased by about 10-20%. (Table 2.3)

Table 2.3 Palladium catalyzed phosphination of aryl bromides with iodide salts



(2.8)

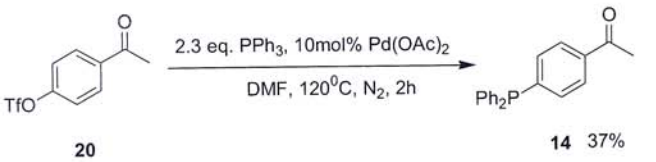
Entry	Product	Salt	Time /h	Yield /%*
1	 **14**	KI	10	60
2	 **16**	KI	16	49
3	 **17**	KI	15	29
4	 **18**	KI	40	34
5	 **19**	KI	12	42
6	 **16**	NaI	48	52

*Isolated yield

Electron-poor aryl bromides (Table 2.3, entry 1, 2, 6) gave higher yields than electron-rich aryl bromides (Table 2.3, entry 3). One possible reason is the oxidation stability of electron deficient phosphines to phosphine oxide is higher than that of electron-rich phosphines.

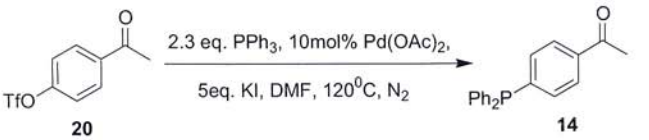
2.2 Iodide effect in phosphination of aryl triflates

The phosphination of 4-acetylphenyl triflate **(20)**, without any salt additive, required 2 hours to yield 4-(diphenylphosphino)acetophenone **(14)** in 37 % (Equation 2.7).[19] Added iodides, however, exhibited an inferior effect in both the rates and yields of the phosphination (Table 2.4 and Table 2.5).



20 **14** 37% (2.9)

Table 2.4 Palladium catalyzed phosphination of aryl triflate with KI



(2.10)

Time /h	Yield /%*	S.M. Consumed /%*
4	0	20
9	0	45
20	0	100
45	20	100
96	40	100

*GC yield

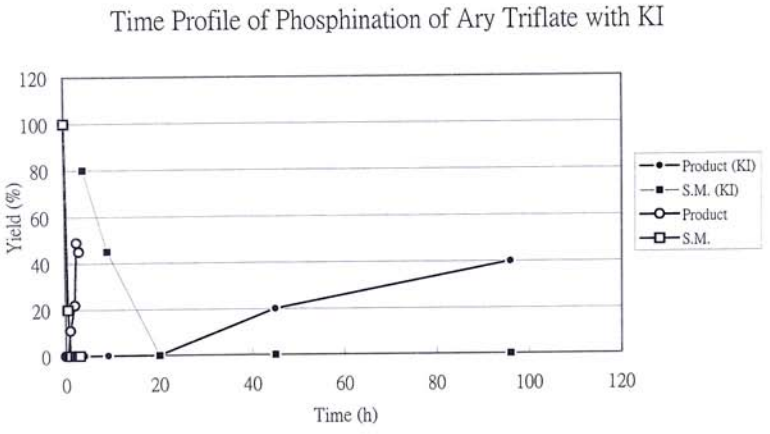
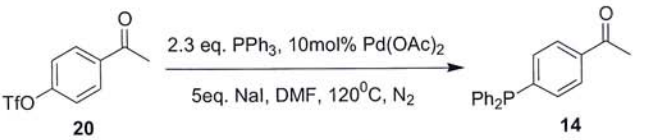


Table 2.5 Palladium Catalyzed Phosphination of Aryl Triflate with NaI



20 14 (2.11)

Time/h	Yield /%*
48	12
96	16

*GC yield

The complete consumption of **20** required 20 hours. The yield of product **14** after 96 hours was obtained in 40 % GC yield. No 4-iodoacetophenone was detected by GC-MS during the reaction. The lack of promoting but rather suppressing effect is likely caused by the reduction in the rate of more coordinating iodide compared to the triflate in the Pd-aryl/P-aryl exchange step,[25] which is very likely the rate determining step of the catalysis. The inferior effect of iodide in oxidative addition also cannot be eliminated.

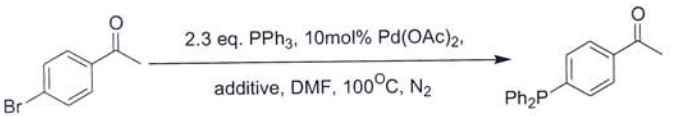
2.3 Low Temperature Phosphination

In an attempt to lower the reaction temperature so as to avoid any undesirable competitive thermal decomposition, reduction or secondary phosphination, the

effect of temperature of phosphination was investigated.

Without any additive, the phosphination at 100^0C required 3 days to give a very low yield of **14**. Addition of 5 equivalents of KI shortened the reaction time to 2.5 days and a higher yield of 58 % was obtained. Et_4NI behaved similarly with KI but $NaBF_4$ exhibited a poorer promoting effect. At 80^0C, KI did not show any promoting effect. Et_4NI, however, showed only a slightly enhancing effect but synthetically unfruitful (Table 2.6). Therefore, the minimal temperature for the phosphination even with the addition of 5 equivalents of KI or Et_4NI required 100^0C.

Table 2.6 Low Temperature Phosphination of 4-Bromoacetophenone



10 **14** (2.12)

Additive	Temp /^{O}C	Time /d	Yield /%
—	115	1	40[18]
—	100	3	12
KI	100	2.5	58
KI	80	3	no reaction
$NaBF_4$	100	5	30
$NaBF_4$	80	5	no reaction
Et_4NI	80	5	22
Et_4NI	100	2.5	58

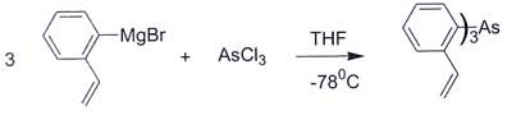
2.4 Conclusion

The catalytic user-friendly palladium-catalyzed phosphination of aryl bromides using triphenylphosphines as the phosphinating reagents was successfully optimized by addition of iodides. This carbon-phosphorus bond formation was compatible with a number of functional groups, including aldehyde, ketone, ester and nitrile group.

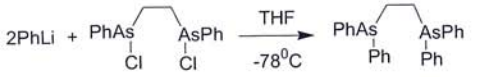
Part II - Syntheses of optically active As, N ligands and their metal complexes

Chapter 1 Introduction

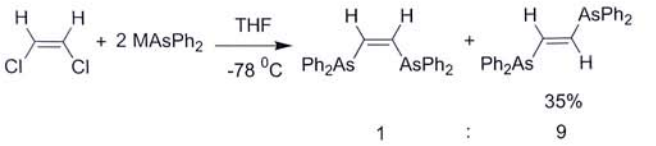
Arsines, analogues of phosphines, are also useful ligands. However, the chemistry of phosphines is much better developed than that of arsines. This may be due to the fact that phosphines can form more stable bondings with transition metals and is much less toxic.[34,35] Similar to the preparation of phosphines, arsines compounds can be synthesized via eletrophilic arsinic reagents (Equation 3.1 and 3.2)[36,37] and nucleophilic arsinic reagents (Equation 3.3).[38]



60% (3.1)[36]



55% (3.2)[37]



(3.3)[38]

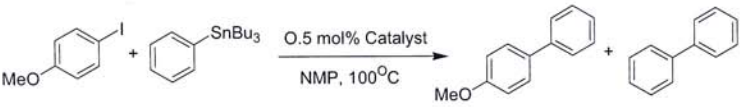
M = Na, K, Li

In catalysis, weaker metal-ligand bond may be beneficial to facilitate the formation of coordinatively unsaturated active catalyst. Examples of arsine ligands in enhancing the reaction yields and rates are reported in Stille,[39] Heck,[40] hydroformylation,[41] carbonylation,[42] epoxidation[43] and olefination reactions.[44,45]

The Stille coupling reaction is one of the most familiarized palladium catalyzed coupling reactions. It is widely used in the total synthesis of large molecules in coupling of complex subunits.[46,47] Recently, studies have revealed that ligand effect and co-catalyst by copper(I) salt improve Stille reactions both in reaction rate and yield.[48]

In one case, the addition of triphenylarsine as a ligand in a Stille reaction gives higher yields of biaryl **22** with much less undesirable homocoupling product, **23**, than the addition of triphenylphosphine as a ligand (Table 3.1).

Table 3.1 Ligand Effect of the Heterogeneous Coupling of **20** and **21**.[49]



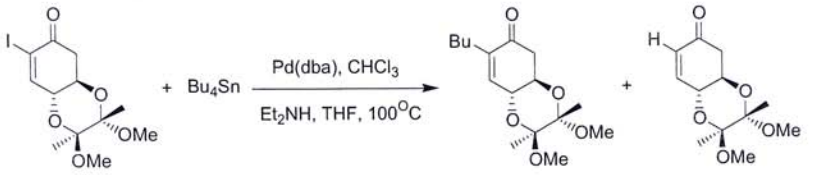
20 **21** **22** **23**

Catalyst	Time	% Yield of **(22)**	% Biphenyl **(23)**
Pd/C	>24h	46	25
Pd/C + 10% CuI	120min	75	12
Pd/C + 10% CuI + 20% $AsPh_3$	21min	88	10
Pd/C + 10% CuI + 20% PPh_3	N/A	<2	90

The addition of triphenylphosphine suppresses the Stille coupling reaction and gives biphenyl as the major product by palladium catalyzed aryl/aryl exchange. It is suggested that the transmetalation from tin to copper is blocked by triphenylphosphine but not triphenylarsine.[49]

The enhancing effect of $AsPh_3$ in Stille reactions can also be observed in alkyl-alky cross coupling (Table 3.2).[50] The addition of phosphine as ligand only gives the reduced product. Amatore has recently revealed that $Pd(AsPh_3)$ and $Pd(PPh_3)_2$ are the major species in solution. Therefore, the higher activity of Pd-arsine catalyst is ascribed to the lower coordination number.[51]

Table 3.2 Stille coupling of 4 with Bu_4Sn

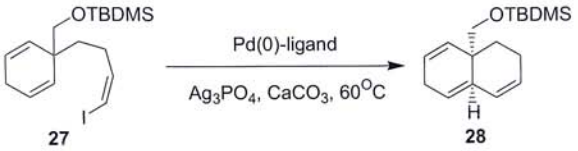


24 **25** **26**

Ligand	Time(h)	CuI	Product	Yield /%
$AsPh_3$	48	Yes	**25**	99
$AsPh_3$	48	No	**25**	97
PPh_3	48	Yes	**26**	63
PPh_3	48	No	**26**	61

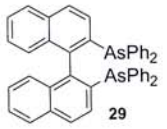
In the palladium catalyzed asymmetric Heck reaction, the use of optically active biarylphosphine ligand, 2,2'-bis(diphenylphosphino)-1-1'-binaphthyl (BINAP), proves to be effective in most cases.[52] However, the low reaction rate and high catalyst loading are still often associated with. Recently, the use of new optically active arsine ligand (BINAs, **29**) has been discovered to be a much more effective ligand in Heck reactions. The use of BINAs in asymmetric Heck reaction of alkenyl iodide not only increases the reaction yield significantly, but also more than twice the enantiomeric excess (Table 3.3).[53]

Table 3.3 Asymmetric Heck Reaction of Alkenyl iodide[53]



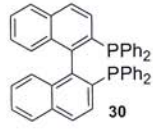
27 28

Pd(0)-ligand	Time /h	Yield /%	ee /%
5 mol% $Pd_2(dba)_3$ + 15 mol% (*R*)-BINAs	24	90	82
5 mol% $Pd_2(dba)_3$ + 15 mol% (*R*)-BINAP	24	55	32
10 mol% Cl_2Pd[(*R*)-BINAP]	84	67	30



29

2,2'-bis(diphenylarsino)-1-1'-binaphthyl (BINAs)

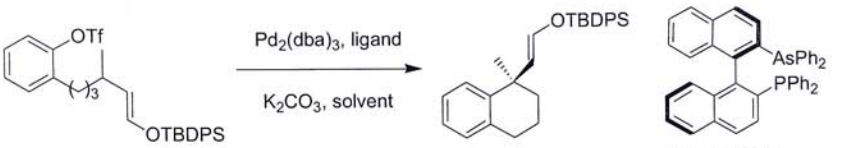


30

2,2'-bis(diphenylphosphino)-1-1'-binaphthyl (BINAP)

The arsine effect is also operating in another Heck reaction. A mixed donor ligand, 2-diphenylarsino-2'-diphenylphosphino-1,1'-binaphthyl (BINAPAs, **33**) increases the reaction yield but lower the % ee value compared to the use of BINAP **(30)** in THF. However, when the solvent is either toluene or 1,2-dichloroethane, the yields improve significantly with little effect on the enantiomeric excess. (Table 3.4).[54]

Table 3.4 Asymetric Heck reaction Using BINAPAs and BINAP

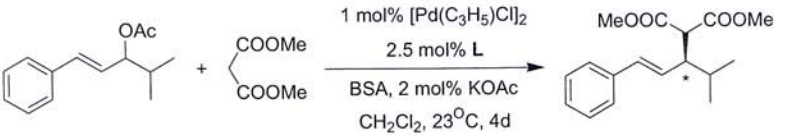


31 **32** (*R*)-BINAPAs **33**

Entry	ligand	solvent	temp /^{O}C	Yield /%	ee /%
1	20 mol% (*R*)-BINAP	THF	60	60	87
2	20 mol% (*R*)-BINAPAs	THF	60	86	61
3	20 mol% (*R*)-BINAP	toluene	40	74	89
4	20 mol% (*R*)-BINAPAs	toluene	40	91	88
5	30 mol% (*R*)-BINAP	$ClCH_2CH_2Cl$	40	73	82
6	30 mol% (*R*)-BINAPAs	$ClCH_2CH_2Cl$	40	88	81

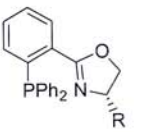
Besides the biaryl ligands, a common ligand type is the phosphinooxazolines.[55,56,57] Metal complexes of phosphinooxazolines such as palladium,[58] platinum,[59] copper,[60,61] rhodium,[62] ruthenium,[63] iridium,[64] molybdenum[65] and tungsten[66] have been used in asymmetric allylic alkylations,[58,59,62,65,66] (Table 3.5 and 3.6) 1,4 additions,[60,61] hydrogenation[67] and Diels-Alder reaction,[62] etc.

Table 3.5 Enantioselective Pd-catalyzed allylic alkylation.



34 **35** **36**

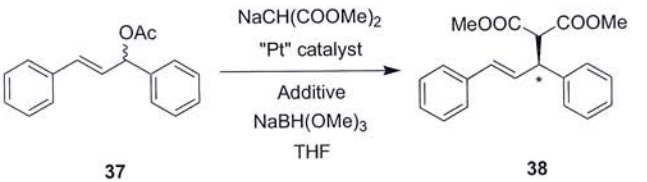
L, R=	Yield /%	ee /%
L1, CH_3	98	89
L2, CH_2Ph	97	97
L3, *i*Pr	98	98
L4, Ph	99	99
L5, *t*Bu	95	94



37,L

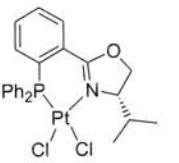
Optically active phosphinooxazoline-chiral ligands **(37)** in metal catalyzed allylic alkylation have been pioneered by Plaftz. The palladium catalyzed allylic alkylation is carried out in mild conditions and compatible with many functional groups.[68] Therefore, it is one of the most efficient and versatile methods of enantioselective carbon-carbon bond and carbon-heteroatom bond formation.[69] The platinum-phosphinooxazoline complex is also shown to be efficient catalyst in allylic alkylation (Table 3.6).[59]

Table 3.6 Enantioselective allylic alkylation with Pt complex



37 **38**

Additive	temp. /°C	time /h	Yield /%	ee /%
—	65	44	65	77
5% **L**	65	35	100	83
10% **L**	65	44	100	61
5% PPh_3	20	16	100	2

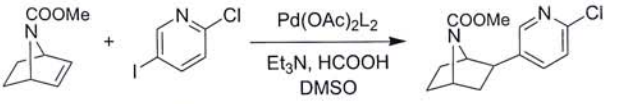


Pt complex, **39**

Modification of this versatile P,N ligand to As,N ligand would provide a novel type of ligand for further application in asymmetric catalysis. A survey of literature reveals that only one reported optically active As,N ligand was synthesized.

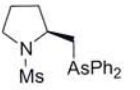
In 1999, Namyslo and co-workers reported a As,N mixed donor ligand **(43)** giving better yield than the use of triphenylphosphine and triphenylarsine as ligands in the preparation of *N*-protected Epibatidine **(42)** via a Heck type hydroarylation. However, the asymmetric induction was poor. [70]

Table 3.7 Heck Type Hydroarylation with Different Ligands.



40 **41** **42**

L	Yield /%
PPh_3	45
$AsPh_3$	81
43	92



43

3.2 The Objective of This Work

Given the unexplored chemistry of optically active As,N ligands, this part of the thesis concerns the syntheses of optically active As, N ligands and their metal complexes.

Part II

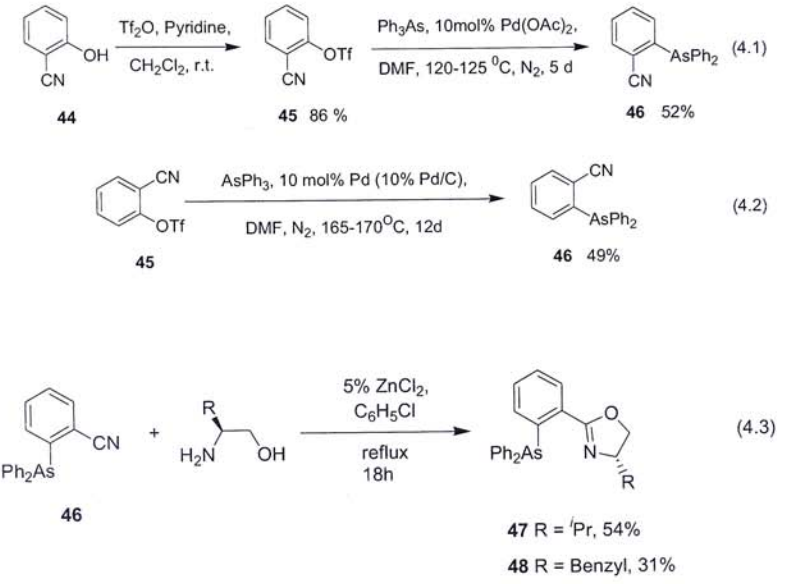
Chapter 2 Synthesis of optically active As, N ligands and their metal complexes

4.1 Synthesis of As,N oxazoline

The extension of palladium catalyzed phosphination to arsination has been reported by Chan's group in 2001.[71] The same synthetic route was adapted to access two derivatives of arsinooxazolines, (*S*)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline **(47)** and (*S*)-2-(2-(diphenylarsino)phenyl)-4-(benzyl)oxazoline **(48)**. Firstly, 2-cyanophenyl trifluoromethanesulfonate **(45)** (Scheme 4.1.1) was prepared from 2-cyanophenol in the presence of pyridine and trifluoromethanesulfonic anhydride in 86% yield.[72] The arsination of 2-cyanophenyl trifluoromethanesulfonate with triphenylarsine serving as the diphenyl arsinating reagent using $Pd(OAc)_2$ or Pd/C catalyst in DMF gave an air stable 2-(diphenylarsino)benzonitrile **(46)** in 52 % and 49 % yield respectively.[71] Finally, the optically active ligands, (*S*)-(+)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline **(47)** and (*S*)-(+)-2-(2-(diphenylarsino)phenyl)-4-(benzyl)oxazoline **(48)**, were obtained by reacting 2-(diphenylarsino)benzonitrile with (*S*)-(+)-2-amino-3-methyl-1-butanol and

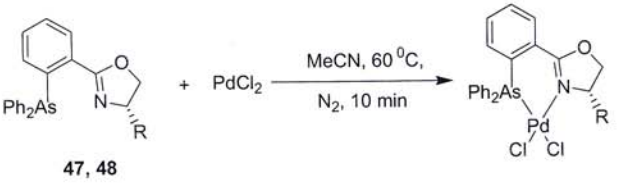
2-amino-3-phenyl-1-propanol in the presence of anhydrous $ZnCl_2$ in chlorobenzene in 54 % and 31 % respectively (Scheme 4.1). **48** might need further optimization.

Scheme 4.1



4.2 Synthesis of As,N-oxazoline transition metal complexes

With the As,N ligands prepared successfully, the As,N oxazolines palladium complexes were synthesized from the reactions of the corresponding As,N oxazolines with 1 equivalent $PdCl_2$ in acetonitrile (Equation 4.4). The products were further purified by recrystallization from CH_2Cl_2/hexane.



(4.4)

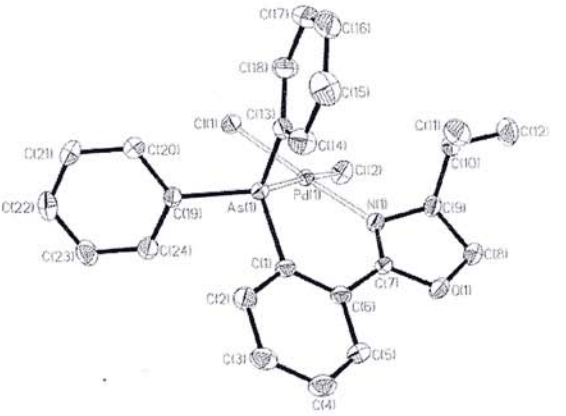
47, 48

49 R = ^{i}Pr, 75%

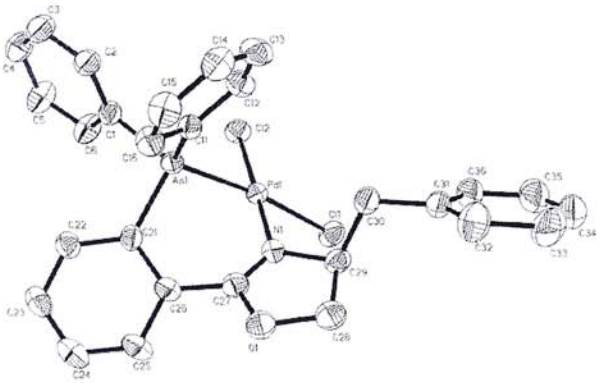
50 R = Benzyl, 76%

The palladium complexes were further characterized by single crystal X-ray crystallography (Figure 4.1). The selected bond lengths and bond angles are listed in Table 4.1 and 4.2.

Figure 4.1



Complex **49**



Complex **50**

Table 4.1 Selected bond lengths and bond angles of complex **49**

Bond lengths (Å)		Bond angles (°)	
Pd (1)—N (1)	2.040 (2)	N (1)—Pd (1)—As (1)	88.36 (7)
Pd (1)—As (1)	2.312 (3)	N (1)—Pd (1)—Cl (1)	173.75 (8)
Pd (1)—Cl (1)	2.289 (8)	N (1)—Pd (1)—Cl (2)	92.67 (8)
Pd (1)—Cl (2)	2.370 (9)	Cl (1)—Pd (1)—As (1)	87.94 (2)
		Cl (2)—Pd (1)—As (1)	174.81 (3)

Table 4.2 Selected bond lengths and bond angles of complex **50**

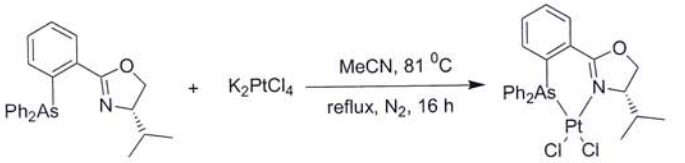
Bond lengths (Å)		Bond angles (°)	
Pd (1)—N (1)	2.040 (6)	N (1)—Pd (1)—As (1)	84.83 (16)
Pd (1)—As (1)	2.334 (8)	N (1)—Pd (1)—Cl (1)	90.22 (17)
Pd (1)—Cl (1)	2.359 (17)	N (1)—Pd (1)—Cl (2)	176.42 (17)
Pd (1)—Cl (2)	2.279 (18)	Cl (1)—Pd (1)—As (1)	172.71 (5)
		Cl (2)—Pd (1)—As (1)	92.17 (5)

The X-ray crystal structure analyses of **49** and **50** reveal that the coordination geometry around the palladium(II) center are slightly distorted square-planar in geometry. The As-Pd-N bite angle of complex of **50** (84.83^0) is smaller than that of **49** (88.36^0). The Pd-As bond length of both complexes exhibit normal As-metal bond length of about 2.3-2.5 Å.[73,74] However, the bond lengths of Pd-Cl bond *cis* to the substitutient on the oxazoline ring in both complexes are longer than that of the Pd-Cl bond where the Cl atom is *trans* to the substitutient on the oxazoline ring. This may

due to the larger *trans*-directing influence of aryl arsine than the imino group.[75]

4.4 Synthesis of Pt-As,N oxazoline complex

The Pt-As,N oxazoline complex was synthesized in a modified procedure. As $PtCl_2$ is not very soluble in acetonitrile, it did not react with **47**. Instead K_2PtCl_4 was dissolved in refluxing acetonitrile and then reacted with **47** under N_2 at 81 ^{0}C for 16 hours to give **51** in 75 %.[76]



47 **51** 75%

4.5 Conclusion

Novel optically active As,N oxazolines, and their palladium and platinum complexes were synthesized. The palladium complexes of *iso*-propyl **(49)** and benzyl **(50)** substituted As, N oxazoline were characterized by single crystal X-ray crystallography. The platinum complex of As, N oxazoline, dichloro[(*S*)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline]platinum(II) **(51)** was synthesized.

Experimental

General Procedures

All materials were obtained from commercial suppliers and used without further purification unless otherwise specified. Toluene was distilled from sodium under N_2. Chloroform was distilled from calcium chloride under N_2. Hexanes were distilled from calcium chloride. Tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium benzophenone ketyl under N_2. Dimethlyformamide was distilled from magnesium sulfate under N_2. Acetonitrile was distilled with P_2O_5 under N_2.

Thin layer chromatography was performed on Merck precoated silica gel 60 F_{254} plates. Column chromatography was performed on silica gel (70-230) or neutral aluminum oxide (activity I, 70-230 mesh).

Anhydrous salts were prepared by heating the salt at 100 ^{0}C under vacuum for overnight.

Physical and Analytical Measurements

^{1}H NMR spectra were recorded on a Bruker DPX-300 (300 MHz). Chemical shifts were referenced with the residual solvent protons in $CDCl_3$ (δ 7.26 ppm) or with tetramethylsilane (δ 0.00 ppm) as the internal standard.

Optical rotation was measured on a Perkin Elmer PE-341 polarimeter at 20 ^{0}C.

Mass spectra were recorded on Hewlett Packard 5989B mass spectrometer (FAB

modes and E.I.) modes at 70 eV or Themo Finnigan MAT 95XL mass spectrometer (FAB mode).

Gas chromatography was performed on a HP G1800 GCD system using a HP5MS column (30 m x 0.25 mm x 0.25 μm), temperature programming: initial temperature 100 °C, duration 2 min.; increment rate 20 °C/min.; final temperature 280 °C, duration 15 min.

4-(Diphenylphosphino)acetophenone (14).[77] 4-Bromoacetophenone (50.0 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6 mg, 0.03 mmol), triphenylphosphine (151.0 mg, 0.58 mmol) and anhydrous NaI (187.4 mg, 1.25 mmol) were dissolved in dry DMF (1.0 mL) under nitrogen in a Teflon Stopcock flask. The solution was degassed and heated to 120-125 °C for 20 hours to yield 4-(diphenylphosphin)acetophenone **(14)** (50.0 mg, 0.15 mmol, 60 %) as a white solid after purification by column chromatography on silica gel eluting with ethyl acetate/hexane (1/20). R_f = 0.22 in ethyl acetate/hexane (1/20); m.p. = 118-120 °C (Lit[77]118-120 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.59 (s, 3 H), 7.31-7.38 (m, 12 H), 7.87 (d, 2 H, J = 8.1 Hz); MS (EI): *m/z* (relative intensity) 304 (M^+, 100), 289 (10), 261 (12), 227 (11), 183 (90), 152 (30).

4-(Diphenylphosphino)benzonitrile (16).[78] 4-Bromobenzonitrile (185.0 mg, 1.0

mmol), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), triphenylphosphine (603.0 mg, 2.3 mmol) and anhydrous NaI (750.0 mg, 5.0 mmol) were dissolved in dry DMF (4.0 mL) under nitrogen in a Teflon Stopcock flask. The solution was degassed and heated to 120-125 °C for 48 hours to yield 4-(diphenylphosphino)benzonitrile **(2)** (149.0 mg, 0.52 mmol, 52 %) as a white solid after purification by column chromatography on silica gel eluting with ethyl acetate/hexane (1/10). R_f = 0.60 ethyl acetate/hexane (1/10); m.p. = 86-87 °C (Lit[78] 86-87 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.39 (m, 12 H), 7.56 (d, 2 H, J = 7.2 Hz). MS (EI): *m/z* (relative intensity) 287 (M^+, 100), 208 (55), 195 (8), 183 (62), 177 (12).

4-(Diphenylphosphino)anisole (17).[77] 4-Bromoanisole (94.0 mg, 0.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), triphenylphosphine (301.0 mg, 1.15 mmol) and anhydrous KI (415.0 mg, 2.5 mmol) were dissolved in dry DMF (2.0 mL) under nitrogen in a Teflon Stopcock flask. The solution was degassed and heated to 120-125 °C for 15 hours to yield 4-(diphenylphosphino)anisole **(17)** (43.0 mg, 0.15 mmol, 29 %) as a white solid after purification by column chromatography on silica gel eluting with ethyl acetate/hexane (1/20). R_f = 0.40 ethyl acetate/hexane (1/20); m.p. = 64.5-65.5°C (Lit[77] 63-65°C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 3 H), 6.90 (d, 2 H, J = 8.1 Hz), 7.25-7.33 (m, 12 H); MS (EI): *m/z* (relative intensity) 292 (M^+, 100),

277 (12), 259 (10), 215 (30), 183 (48).

4-(Diphenylphosphino)benzaldehyde (18).[78] 4-Bromobenzoaldehyde (185.0 mg, 1.0 mmol), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), triphenylphosphine (602.0 mg, 2.3 mmol) and anhydrous KI (830.0 mg, 5.0 mmol) were dissolved in dry DMF (4.0 mL) under nitrogen in a Teflon Stopcock flask. The solution was degassed and heated to 120-125 °C for 40 hours to yield the 4-(diphenylphosphino)benzaldehyde **(18)** (100.0 mg, 0.34 mmol, 34 %) as a white solid after purification by column chromatography on silica gel eluting with ethyl acetate/hexane (1/10); R_f = 0.60 ethyl acetate/hexane (1/10); m.p. = 75.5-77 °C (Lit[78] 69-71 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.43 (m, 12 H), 7.80 (d, 2 H, J = 8.1 Hz), 10.00 (s, 1 H); MS (EI): *m/z* (relative intensity) 290 (M^+, 100), 261 (8), 211 (9), 183 (95), 165 (12), 152 (20).

3-(Diphenylphosphino)anisole (19).[79] 3-Bromoanisole (94.0 mg, 0.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), triphenylphosphine (301.0 mg, 1.15 mmol) and anhydrous KI (415.0 mg, 2.5 mmol) were dissolved in dry DMF (2.0 mL) under nitrogen in a Teflon Stopcock flask. The solution was degassed and heated to 120-125 °C for 12 hours to yield 3-(diphenylphosphino)anisole **(5)** (62.0 mg, 0.21 mmol, 42 %) as a colorless liquid after purification by column chromatography on silica gel

eluting with ethyl acetate/hexane (1/20); R_f = 0.40 ethyl acetate/hexane (1/20); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.72 (s, 3 H), 6.85-6.89 (m, 3H), 7.23-7.35 (m, 11 H); MS (EI): *m/z* (relative intensity) 292 (M^+, 100), 213 (22), 259 (10), 199 (20), 183 (48).

4-Acetylphenyltrifluoromethanesulfonate (20).[72] 4-Hydroxyacetophenone (2.7 g, 20.0 mmol) was dissolved in dry CH_2Cl_2 (100.0 mL) under nitrogen at room temperature followed by the addition of dry pyridine (4.8 mL, 40.0 mmol). Trifluoromethanesulfonic anhydride (3.7 mL, 22.0 mmol) in dry CH_2Cl_2 was then added dropwisely. The color of the solution changed from orange to brown with white fume evolved. The reaction mixture was then stirred at room temperature for 1 hour. Water (50 mL) was then added and the reaction mixture was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phase was washed with dilute hydrochloric acid, water, brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The product was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1/10) to yield 4-acetylphenyltrifluoromethanesulfonate **(20)** (4.6 g, 17.4 mmol, 87 %) as a colorless liquid; R_f = 0.41 ethyl acetate/hexane (1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.65 (s, 3 H), 7.43 (d, 2 H, J = 8.7 Hz), 8.00 (d, 2 H, J = 8.4 Hz). MS (EI): m/z (relative intensity) 268 (M^+, 48), 189 (100), 161 (42).

2-Cyanophenyl trifluoromethanesulfonate (45).[71] 2-Cyanophenol (0.6 g, 5.0 mmol) was dissolved in dry CH_2Cl_2 (20.0 mL) under nitrogen at room temperature followed by the addition of dry pyridine (1.2 mL, 15.0 mmol). Trifluoromethanesulfonic anhydride (1.0 mL, 5.5 mmol) in dry CH_2Cl_2 (10.0 mL) was then added dropwisely. The color of the solution changed from orange to brown with white fume evolved. The reaction mixture was then stirred at room temperature for 1 hour. Water (20 mL) was then added and the reaction mixture was extracted with dichloromethane (3 x 15 mL). The combined organic phase was washed with dilute hydrochloric acid, water, brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The product was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1/10) to yield 2-Cyanophenyl trifluoromethanesulfonate **(45)** (1.1 g, 4.3 mmol, 86 %) as a pale yellow liquid. R_f = 0.61 ethyl acetate/hexane (1/5); ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, 1 H, J = 8.7 Hz), 7.56 (dd, 2 H, J = 0.9, 7.7 Hz), 7.74 (dd, 1 H, J = 1.7, 8.1 Hz), 7.79 (dd, 1 H, J = 1.6, 6.7 Hz).

2-(Diphenylarsino)benzonitrile (46).[71] *Method A* 2-Cyanophenyl trifluoromethanesulfonate (251.0 mg, 1.0 mmol), triphenylarsine (706.0 mg, 2.3 mmol) and $Pd(OAc)_2$ (22.0 mg, 0.1 mmol) were dissolved in dry DMF (4.0 mL) under nitrogen in a Teflon Stopcock flask. The solution was degassed and heated to

120-125 °C for 5 days to yield 2-(diphenylarsino)benzonitrile **(46)** (172.0 mg, 0.52 mmol, 52 %) as a white solid after purification by column chromatography on silica gel eluting with ethyl acetate/hexane (1/5). R_f= 0.51 ethyl acetate/hexane (1/5); m.p. = 112-113 °C (Lit[72] = 111.5-112.5 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, 1 H, *J* = 6.5 Hz), 7.31-7.47 (m, 12 H), 7.69 (d, 1 H, *J* = 6.7 Hz); MS (EI): *m/z* (relative intensity) 331 (M^+, 20), 252 (12), 227 (17), 177 (21), 152 (100).

Method B 2-Cyanophenyl trifluoromethanesulfonate (251.0 mg, 1.0 mmol), triphenylarsine (706.0 mg, 2.3 mmol) and 10 % Pd/C (106.0 mg, 0.1 mmol) were suspended in dry DMF (4.0 mL) under nitrogen in a Teflon Stopcock flask. The solution was degassed and heated to 120-125 °C for 12 days to yield 2-(diphenylarsino)benzonitrile **(46)** (162 mg, 0.49 mmol, 49 %) as a white solid after purification by column chromatography on silica gel eluting with ethyl acetate/hexane (1/5).

(*S*)-(-)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline (47).

2-(Diphenylarsino)benzonitrile (25.0 mg, 0.08 mmol), anhydrous zinc(II) chloride (11.7 mg, 0.11 mmol) and (*S*)-(+)-2-amino-3-methyl-1-butanol (11.7 mg, 0.11 mmol) were dissolved in dry chlorobenzene (0.5 mL) and heated to reflux at 140 °C under N_2 for 18 hours to yield (*S*)-(-)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline **(47)**

(17 mg, 0.04 mmol , 54 %) as a white solid after purification by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (1/1). It was further recrystallized from CH_2Cl_2/hexane; R_f = 0.43 hexane/CH_2Cl_2 (1/1); m.p. = 140-141 ^oC (Lit.[72] = 140-141.5 ^oC). ^1H NMR (300 MHz, $CDCl_3$) δ 0.71 (d, 3 H, J = 6.6 Hz), 0.82 (d, 3 H, J = 6.6 Hz), 1.21 (s, 1 H), 3.84-3.90 (m, 2 H), 4.16 (p, 1 H, 6.3 Hz), 6.99 (dd, 1 H, J = 1.2, 7.5 Hz), 7.28-7.39 (m, 12 H), 7.91 (dd, 1 H, J = 1.2, 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ18.3, 18.8, 32.6, 70.4, 128.1, 128.2, 128.5, 129.8, 131.0, 131.5, 133.7, 134.0, 134.5, 141.1, 141.5; MS (EI): *m/z* (relative intensity) 418 (M^+, 50), 340 (100), 254 (20); HRMS (ESIMS) Calcd for $C_{24}H_{24}AsNOH^+$, 418.1147; Found 418.1143; $[\alpha]_D^{20}$ = -33.6 (c = 0.06, MeCN).

(*S*)-2-(2-(diphenylarsino)phenyl)-4-(benzyl)oxazoline (48).

2-(Diphenylarsino)benzonitrile (25.0 mg, 0.08 mmol), anhydrous zinc(II) chloride (11.7 mg, 0.11 mmol) and (*S*)-(-)-2-amino-3-phenyl-1-propanol (16.6 mg, 0.11 mmol) were dissolved in chlorobenzene (0.5 mL) and heated to reflux at 140 ^0C under N_2 for 18 hours to yield (*S*)-2-(2-(diphenylarsino)phenyl)-4-(benzyl)oxazoline **(48)** (10.6 mg, 0.02 mmol , 31 %) as a white solid after purification by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (1/1); It was further recrystallized from CH_2Cl_2/hexane; R_f=0.34 CH_2Cl_2/hexane (1/1); m.p. = 153-154 ^oC; ^1H NMR (300

MHz, $CDCl_3$) δ 2.11 (dd, 1 H, J = 9.0, 13.8 Hz), 2.86 (dd, 1 H, J = 5.4, 13.8 Hz), 3.78 (t, 1 H, J = 8.4 Hz), 4.05 (t, 1 H, J = 8.4 Hz), 4.31 (~quint, 1 H, J = 5.4 Hz), 7.00 (d, 1 H, J = 7.5 Hz), 7.06 (d, 2 H, J = 6.6 Hz), 7.18-7.25 (m, 4 H), 7.28-7.39 (m, 11 H), 7.89 (d, 1 H, J = 7.5 Hz); ^{13}C NMR (75MHz, $CDCl_3$) δ 29.7, 41.1, 68.0, 71.5, 126.3, 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, 129.1, 129.7, 130.8, 131.8, 133.7, 134.2, 134.4, 138.2, 141.2, 141.3, 141.8; MS (EI): *m/z* (relative intensity) 466 (M^+, 30), 388 (100), 256 (15); HRMS (ESIMS) Calcd for $C_{28}H_{24}AsNOH^+$, 466.1147; Found 466.1147; Elemental Analysis: Calcd for %C 72.26, %H 5.20, %N 3.01; Found %C 72.18, %H 5.55, %N 2.82; $[\alpha]_D^{20}$ = 12.5 (c = 0.20, MeCN).

Dichloro[(*S*)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline]palladium(*II*) (49). A solution of (*S*)-(+)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline (15.0 mg, 0.04 mmol) in acetonitrile (0.5 mL) was added to a clear orange mixture of $PdCl_2$ (6.4 mg, 0.04 mmol) in acetonitrile (0.5 mL) at 60 ^{0}C and stirred for 10 minutes. The color changed from orange to yellow. The solution mixture was then cooled to room temperature. Yellow precipitate was formed and was collected by filtration, washed with cold acetonitrile and then diethyl ether to give dichloro[(*S*)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline]palladium(*II*) **(49)** (16.1 mg, 0.03 mmol, 75 %) as a yellow solid. Single crystals were grown from

$CHCl_3$/hexane for X-ray crystallographic analysis. ^1H NMR (300 MHz, $CDCl_3$) δ 0.13 (d, 3 H, J = 6.9 Hz), 0.83 (d, 3 H, J = 6.9 Hz), 2.76 (dt, 1 H, J = 2.7, 7.0 Hz), 4.33 (dd, 1 H, J = 5.1, 9.2 Hz), 4.44 (t, 1 H, J = 9.2 Hz) 5.51 (~dquint, 1 H, J = 1.8, 5.2 Hz), 7.10 (d, 1 H, J = 7.6 Hz), 7.43-7.68 (m, 12 H), 8.11 (d, 1 H, J = 7.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.3, 18.6, 30.8, 68.7, 71.7, 128.7, 128.8, 128.9, 129.2, 129.7, 131.6, 132.0, 132.7, 133.0, 133.5, 133.7,133.8; MS (EI): *m/z* (relative intensity) 593 (M^+, 5), 558 (100), 523 (20), 460 (20); HRMS (ESIMS) Calcd for $C_{24}H_{24}AsNOPdCl^+$, 557.9792; Found 557.9804; Elemental Analysis: Calcd for %C 48.47, %H 4.07, %N 2.36; Found %C 47.96, %H 3.86, %N 2.10; $[\alpha]_D^{20}$ = 290.5 (c = 0.07, MeCN).

Dichloro[(*S*)-2-(2-(diphenylarsino)phenyl)-4-(benzyl)oxazoline]palladium(II) (50)

A solution of (*S*)-(+)-2-(2-(diphenylarsino)phenyl)-4-(benzyl)oxazoline (15.0 mg, 0.03 mmol) in acetonitrile (0.5 mL) was added to a clear orange mixture of $PdCl_2$ (5.7 mg, 0.03 mmol) in acetonitrile (0.5 mL) at 60 ^0C and stirred for 5 minutes. The color changed from orange to yellow. Yellow precipitate formed and the reaction mixture was cooled to room temperature. The yellow precipitate was collected by filtration, washed with cold acetonitrile and then diethyl ether to give dichloro[(***S***)-2-(2-(diphenylarsino)phenyl)-4-(benzyl)oxazoline]palladium(II) **(50)**

(15.7 mg, 0.02 mmol, 76 %) as a yellow solid. Single crystals were grown from $CHCl_3$/hexane for X-ray crystallography analysis. ^1H NMR (300 MHz, $CDCl_3$) δ 1.82 (t, 1 H, J = 11.1 Hz), 3.95 (dd, 1 H, J = 3.8, 13.2 Hz), 4.26 (dd, 1 H, J = 4.8, 8.9 Hz), 4.34 (t, 1 H, J = 9.4 Hz), 5.72 (~dquint, 1 H, J = 2.1, 3.9 Hz), 7.14 (d, 1 H, J = 7.0 Hz), 7.20 (s, 5 H), 7.68-7.44 (m, 12 H), 8.09 (d, 1 H, J = 7.8 Hz); ^{13}C NMR (75MHz, $CDCl_3$) δ 41.0, 68.3, 72.0, 125.9, 127.1, 128.5, 128.7, 129.4, 129.9, 131.8, 132.0, 132.5, 133.1, 133.2, 133.8, 133.9, 135.6; MS (EI): *m/z* (relative intensity) 641 (M^+, 2), 606 (100), 573 (50), 530 (50); HRMS (ESIMS) Calcd for $C_{28}H_{24}AsNOPdCl^+$, 605.9792; Found 605.9802; Elemental Analysis: Calcd for %C 52.32, %H 3.76, %N 2.18; Found %C 52.39, %H 3.53, %N 1.98; $[\alpha]_D^{20}$ = 215.1 (c = 0.015, CH_2Cl_2).

Dichloro[(*S*)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline]platinum(II) (51). A solution of (*S*)-(+)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline (15.0 mg, 0.04 mmol) in acetonitrile (0.5 mL) was added to a mixture of potassium tetrachloroplatinate(II) (15.0 mg, 0.04 mmol) in acetonitrile (0.5 mL). The solution was heated to reflux at 85 ^0C under N_2. After 16 hours, a mixture of yellowish and white precipitate formed and the reaction mixture was cooled to room temperature. The yellow precipitate was collected by filtration, washed with cold acetonitrile and then diethyl ether to give

dichloro[(*S*)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline]platinum(II) **(51)** (17.9 mg, 0.03 mmol, 73 %). The product was further recrystallized from CH_2Cl_2/hexane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.10 (d, 3 H, J = 6.9 Hz), 0.84 (d, 3 H, J = 6.9 Hz), 2.86 (dt, 1 H, J = 3.6, 9.7 Hz), 4.34 (dd, 1 H, J = 4.9, 9.2 Hz), 4.43 (t, 1 H, J = 9.96 Hz), 5.71 (~dquint, 1 H, J = 2.3, 5.1 Hz), 7.15 (d, 1 H, J = 7.4 Hz), 7.40-7.80 (m, 12 H), 8.10 (d, 1 H, J = 7.8 Hz); ^{13}C NMR (75MHz, $CDCl_3$) δ 12.9, 18.4, 18.5, 30.5, 129.1, 129.6, 131.5, 131.8, 132.9, 133.4, 133.5, 133.6; MS (EI): *m/z* (relative intensity) 682 (M^+, 5), 646 (100), 534 (50), 457 (50); HRMS (ESIMS) Calcd for $C_{24}H_{24}AsNOPtCl^+$, 647.0405; Found 647.0405; Elemental Analysis: Calcd for %C 42.18, %H 3.54, %N 2.05; Found %C 42.08, %H 3.84, %N 1.86; $[\alpha]_D^{20}$ = 217.9 (c = 0.015, CH_2Cl_2).

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Appendix

Dichloro[(*S*)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline]palladium(II) (49)

Table 1. Crystal data and structure refinement

Identification code	p21
Empirical formula	$C_{25}H_{26}AsCl_4NOPd$
Formula weight	679.59
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 10.3397(5) Å alpha = 90° b = 12.8918(6) Å beta = 112.029(1)° c = 10.8073(5) Å gamma = 90°
Volume, Z	1335.4(1) $Å^3$, 2
Density (calculated)	1.690 Mg/m^3
Absorption coefficient	2.344 mm^{-1}
F(000)	676
Crystal size	0.64 x 0.60 x 0.52 mm
θ range for data collection	2.03 to 27.99°
Limiting indices	$-13 \le h \le 13$, $-17 \le k \le 16$, $-14 \le l \le 6$
Reflections collected	8883
Independent reflections	6067 (R_{int} = 0.0258)
Completeness to θ = 27.99°	99.6 %
Absorption correction	SADABS
Max. and min. transmission	1.0000 and 0.7604
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6067 / 1 / 299
Goodness-of-fit on F^2	1.056
Final R indices [I>2σ(I)]	R1 = 0.0256, wR2 = 0.0692
R indices (all data)	R1 = 0.0266, wR2 = 0.0696
Absolute structure parameter	0.024(7)
Extinction coefficient	0.0012(5)

Table 3. Bond lengths [Å] and angles [°]

N(1)-C(7)	1.293(4)	N(1)-C(9)	1.493(4)
N(1)-Pd(1)	2.040(2)	Pd(1)-Cl(1)	2.2891(8)
Pd(1)-As(1)	2.3122(3)	Pd(1)-Cl(2)	2.3697(9)
As(1)-C(13)	1.928(3)	As(1)-C(19)	1.932(3)
As(1)-C(1)	1.935(3)	C(1)-C(6)	1.386(5)
C(1)-C(2)	1.398(5)	C(2)-C(3)	1.391(5)
C(3)-C(4)	1.381(6)	C(4)-C(5)	1.365(6)
C(5)-C(6)	1.401(4)	C(6)-C(7)	1.486(4)
C(7)-O(1)	1.333(4)	C(8)-O(1)	1.461(5)
C(8)-C(9)	1.524(5)	C(9)-C(10)	1.528(5)
C(10)-C(11)	1.521(7)	C(10)-C(12)	1.544(6)
C(13)-C(14)	1.384(5)	C(13)-C(18)	1.393(5)
C(14)-C(15)	1.395(6)	C(15)-C(16)	1.369(7)
C(16)-C(17)	1.376(7)	C(17)-C(18)	1.385(5)
C(19)-C(24)	1.377(5)	C(19)-C(20)	1.396(5)
C(20)-C(21)	1.389(5)	C(21)-C(22)	1.378(6)
C(22)-C(23)	1.376(6)	C(23)-C(24)	1.381(5)
Cl(3)-C(25)	1.751(7)	Cl(4)-C(25)	1.733(7)

C(7)-N(1)-C(9)	108.4(3)	C(7)-N(1)-Pd(1)	133.5(2)
C(9)-N(1)-Pd(1)	118.1(2)	N(1)-Pd(1)-Cl(1)	173.75(8)
N(1)-Pd(1)-As(1)	88.36(7)	Cl(1)-Pd(1)-As(1)	87.94(2)
N(1)-Pd(1)-Cl(2)	92.67(8)	Cl(1)-Pd(1)-Cl(2)	91.46(3)
As(1)-Pd(1)-Cl(2)	174.81(3)	C(13)-As(1)-C(19)	108.69(13)
C(13)-As(1)-C(1)	104.63(13)	C(19)-As(1)-C(1)	103.05(14)
C(13)-As(1)-Pd(1)	112.08(9)	C(19)-As(1)-Pd(1)	117.01(9)
C(1)-As(1)-Pd(1)	110.33(10)	C(6)-C(1)-C(2)	120.0(3)
C(6)-C(1)-As(1)	122.1(2)	C(2)-C(1)-As(1)	117.9(2)
C(3)-C(2)-C(1)	120.3(3)	C(4)-C(3)-C(2)	119.5(3)
C(5)-C(4)-C(3)	120.2(3)	C(4)-C(5)-C(6)	121.5(4)
C(1)-C(6)-C(5)	118.5(3)	C(1)-C(6)-C(7)	123.9(3)
C(5)-C(6)-C(7)	117.4(3)	N(1)-C(7)-O(1)	116.2(3)
N(1)-C(7)-C(6)	130.1(3)	O(1)-C(7)-C(6)	113.6(3)
O(1)-C(8)-C(9)	104.9(3)	N(1)-C(9)-C(8)	102.2(3)
N(1)-C(9)-C(10)	111.9(3)	C(8)-C(9)-C(10)	115.5(3)
C(11)-C(10)-C(9)	114.5(4)	C(11)-C(10)-C(12)	111.5(4)
C(9)-C(10)-C(12)	108.9(4)	C(14)-C(13)-C(18)	120.3(3)
C(14)-C(13)-As(1)	122.2(3)	C(18)-C(13)-As(1)	117.3(3)
C(13)-C(14)-C(15)	118.8(4)	C(16)-C(15)-C(14)	121.1(4)
C(15)-C(16)-C(17)	119.7(4)	C(16)-C(17)-C(18)	120.7(4)
C(17)-C(18)-C(13)	119.4(4)	C(24)-C(19)-C(20)	119.9(3)
C(24)-C(19)-As(1)	119.3(2)	C(20)-C(19)-As(1)	120.7(2)
C(21)-C(20)-C(19)	119.1(4)	C(22)-C(21)-C(20)	120.3(4)
C(23)-C(22)-C(21)	120.3(3)	C(22)-C(23)-C(24)	119.9(4)
C(19)-C(24)-C(23)	120.4(4)	C(7)-O(1)-C(8)	107.3(2)
Cl(4)-C(25)-Cl(3)	113.3(4)		

Symmetry transformations used to generate equivalent atoms:

Dichloro[(*S*)-2-(2-(diphenylarsino)phenyl)-4-(benzyl)oxazoline]palladium(II) (50)

Table 1. Crystal data and structure refinement for P.

Identification code	my175
Empirical formula	$C_{28}H_{24}AsCl_2NOPd$
Formula weight	642.70
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	MONCLINIC
Space group	$P2_1$
Unit cell dimensions	a = 8.9267(18) Å alpha = 90° b = 10.333(2) Å beta = 105.58(3)° c = 14.669(3) Å gamma = 90°
Volume, Z	1303.3(5) $Å^3$, 2
Density (calculated)	1.638 Mg/m^3
Absorption coefficient	2.198 mm^{-1}
F(000)	640
Crystal size	0.35 x 0.20 x 0.10 mm
θ range for data collection	1.44 to 25.71°
Limiting indices	$0 \le h \le 10$, $-12 \le k \le 12$, $-17 \le l \le 17$
Reflections collected	4061
Independent reflections	3940 (R_{int} = 0.0501)
Completeness to θ = 25.71°	95.4 %
Absorption correction	ABSCOR
Max. and min. transmission	1.000 and 0.876
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3940 / 1 / 310
Goodness-of-fit on F^2	0.984
Final R indices [I>2σ(I)]	R1 = 0.0416, wR2 = 0.1152
R indices (all data)	R1 = 0.0419, wR2 = 0.1183
Absolute structure parameter	0.357(15)
Largest diff. peak and hole	0.404 and -0.978 $eÅ^{-3}$

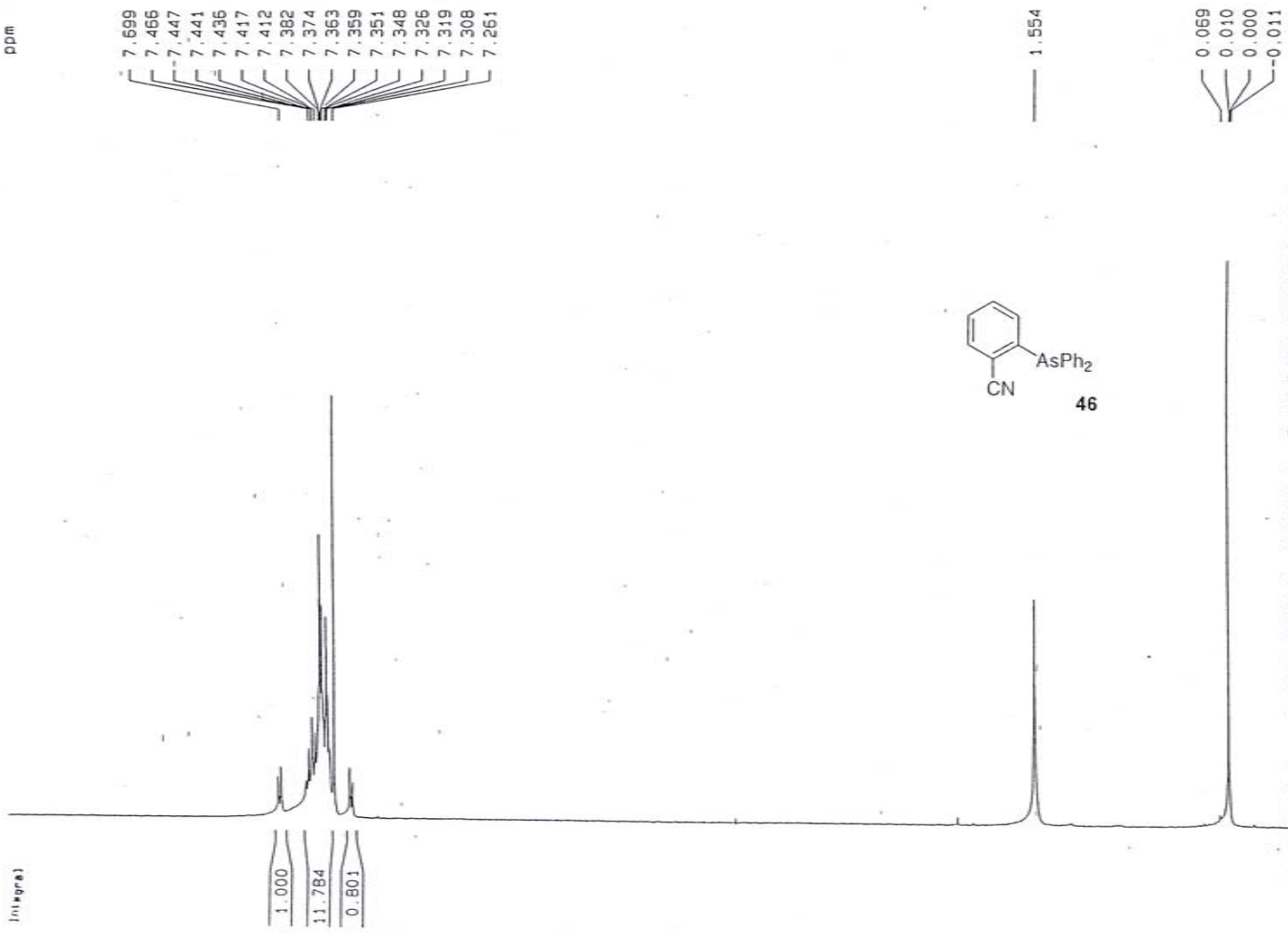
Table 3. Bond lengths [Å] and angles [°] for P.

Pd(1)-N(1)	2.040(6)	Pd(1)-Cl(2)	2.2789(18)
Pd(1)-As(1)	2.3342(8)	Pd(1)-Cl(1)	2.3589(17)
As(1)-C(11)	1.922(6)	As(1)-C(21)	1.921(7)
As(1)-C(1)	1.942(6)	C(1)-C(2)	1.381(9)
C(1)-C(6)	1.387(9)	C(16)-C(15)	1.394(11)
C(16)-C(11)	1.400(11)	O(1)-C(27)	1.340(9)
O(1)-C(28)	1.464(12)	C(29)-N(1)	1.495(9)
C(29)-C(30)	1.529(11)	C(29)-C(28)	1.537(12)
N(1)-C(27)	1.282(10)	C(27)-C(26)	1.456(10)
C(5)-C(4)	1.394(12)	C(5)-C(6)	1.403(11)
C(2)-C(3)	1.397(10)	C(26)-C(25)	1.410(10)
C(26)-C(21)	1.435(9)	C(25)-C(24)	1.376(13)
C(4)-C(3)	1.365(12)	C(21)-C(22)	1.385(10)
C(23)-C(22)	1.388(11)	C(23)-C(24)	1.387(13)
C(11)-C(12)	1.394(10)	C(31)-C(36)	1.380(13)
C(31)-C(32)	1.390(14)	C(31)-C(30)	1.497(10)
C(15)-C(14)	1.356(14)	C(12)-C(13)	1.359(11)
C(13)-C(14)	1.392(14)	C(36)-C(35)	1.371(15)
C(32)-C(33)	1.50(2)	C(35)-C(34)	1.31(2)
C(34)-C(33)	1.36(3)		

N(1)-Pd(1)-Cl(2)	176.42(17)	N(1)-Pd(1)-As(1)	84.83(16)
Cl(2)-Pd(1)-As(1)	92.17(5)	N(1)-Pd(1)-Cl(1)	90.22(17)
Cl(2)-Pd(1)-Cl(1)	92.94(7)	As(1)-Pd(1)-Cl(1)	172.71(5)
C(11)-As(1)-C(21)	104.6(3)	C(11)-As(1)-C(1)	104.6(3)
C(21)-As(1)-C(1)	104.8(3)	C(11)-As(1)-Pd(1)	113.79(19)
C(21)-As(1)-Pd(1)	102.17(18)	C(1)-As(1)-Pd(1)	124.8(2)
C(2)-C(1)-C(6)	120.8(6)	C(2)-C(1)-As(1)	119.9(5)
C(6)-C(1)-As(1)	119.3(5)	C(15)-C(16)-C(11)	117.9(8)
C(27)-O(1)-C(28)	107.3(6)	N(1)-C(29)-C(30)	110.9(6)
N(1)-C(29)-C(28)	102.7(6)	C(30)-C(29)-C(28)	116.8(7)
C(27)-N(1)-C(29)	108.5(6)	C(27)-N(1)-Pd(1)	130.3(5)
C(29)-N(1)-Pd(1)	121.2(5)	N(1)-C(27)-O(1)	116.8(7)
N(1)-C(27)-C(26)	127.7(7)	O(1)-C(27)-C(26)	115.5(6)
O(1)-C(28)-C(29)	104.4(6)	C(4)-C(5)-C(6)	120.5(7)
C(1)-C(2)-C(3)	119.7(7)	C(25)-C(26)-C(21)	118.9(7)
C(25)-C(26)-C(27)	118.9(7)	C(21)-C(26)-C(27)	122.2(6)
C(1)-C(6)-C(5)	118.6(6)	C(24)-C(25)-C(26)	120.7(8)
C(3)-C(4)-C(5)	119.6(7)	C(22)-C(21)-C(26)	118.8(7)
C(22)-C(21)-As(1)	122.4(5)	C(26)-C(21)-As(1)	118.8(5)
C(22)-C(23)-C(24)	120.9(8)	C(25)-C(24)-C(23)	119.9(8)
C(23)-C(22)-C(21)	120.7(7)	C(4)-C(3)-C(2)	120.7(7)
C(12)-C(11)-C(16)	120.1(6)	C(12)-C(11)-As(1)	119.5(5)
C(16)-C(11)-As(1)	120.3(5)	C(36)-C(31)-C(32)	120.0(9)
C(36)-C(31)-C(30)	119.0(8)	C(32)-C(31)-C(30)	121.0(9)
C(14)-C(15)-C(16)	121.1(8)	C(31)-C(30)-C(29)	112.0(6)
C(13)-C(12)-C(11)	120.8(8)	C(12)-C(13)-C(14)	119.0(8)
C(35)-C(36)-C(31)	122.2(12)	C(31)-C(32)-C(33)	115.0(13)
C(34)-C(35)-C(36)	120.8(15)	C(35)-C(34)-C(33)	121.5(13)
C(15)-C(14)-C(13)	121.1(6)	C(34)-C(33)-C(32)	120.5(12)

Symmetry transformations used to generate equivalent atoms:

my 76.1



Current Data Parameters

NAME	my76.1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20020205
Time	12.24
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	16
DS	0
SWH	8992.806 Hz
FIDRES	0.274439 Hz
AQ	1.8219508 sec
RG	1024
DW	55.600 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 =======

NUC1	1H
P1	4.50 usec
PL1	-2.00 dB
SFO1	300.1312000 MHz

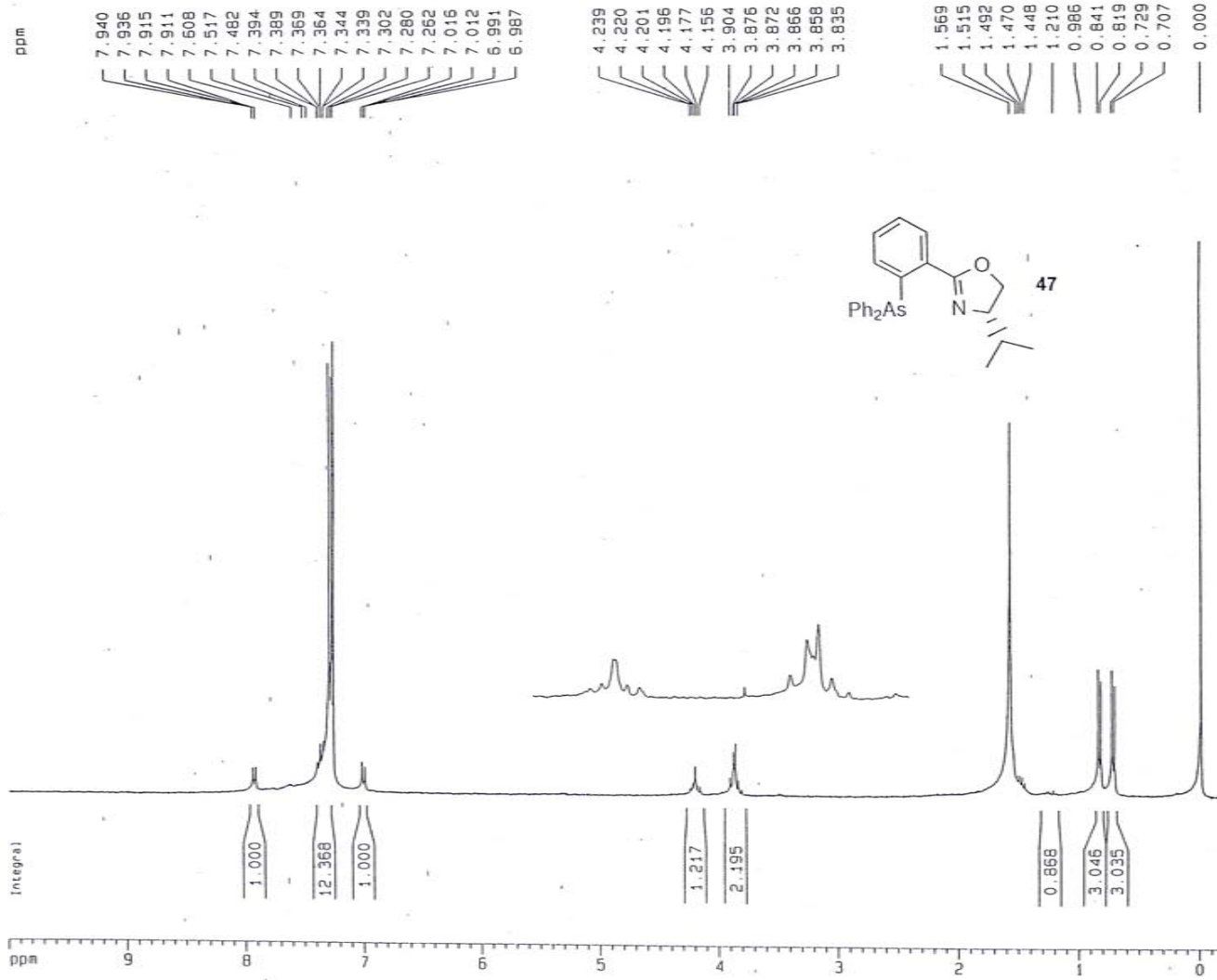
F2 - Processing parameters

SI	32768
SF	300.1300065 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm

my171



Current Data Parameters

NAME	my171
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20020916
Time	20.54
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	16
DS	0
SWH	8992.806 Hz
FIDRES	0.274439 Hz
AQ	1.8219508 sec
RG	1149.4
DW	55.600 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 =======

NUC1	1H
P1	4.50 usec
PL1	-2.00 dB
SFO1	300.1312000 MHz

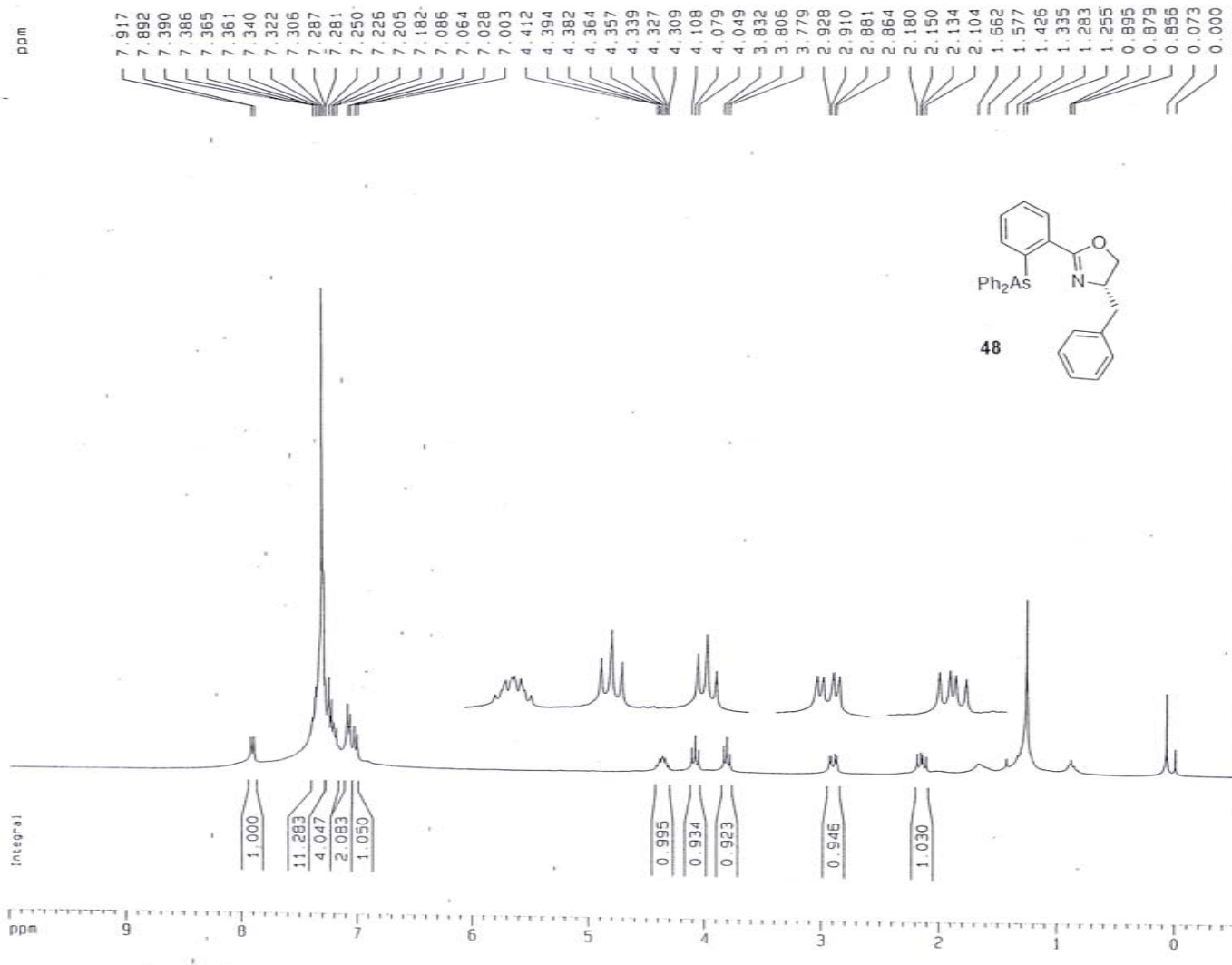
F2 - Processing parameters

SI	32768
SF	300.1300056 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm

my132



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Current Data Parameters

NAME	my132
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20020726
Time	18.23
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	16
DS	0
SWH	8992.806 Hz
FIDRES	0.274439 Hz
AQ	1.8219508 sec
RG	181
DW	55.600 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 =======

NUC1	1H
P1	4.50 usec
PL1	-2.00 dB
SFO1	300.1312000 MHz

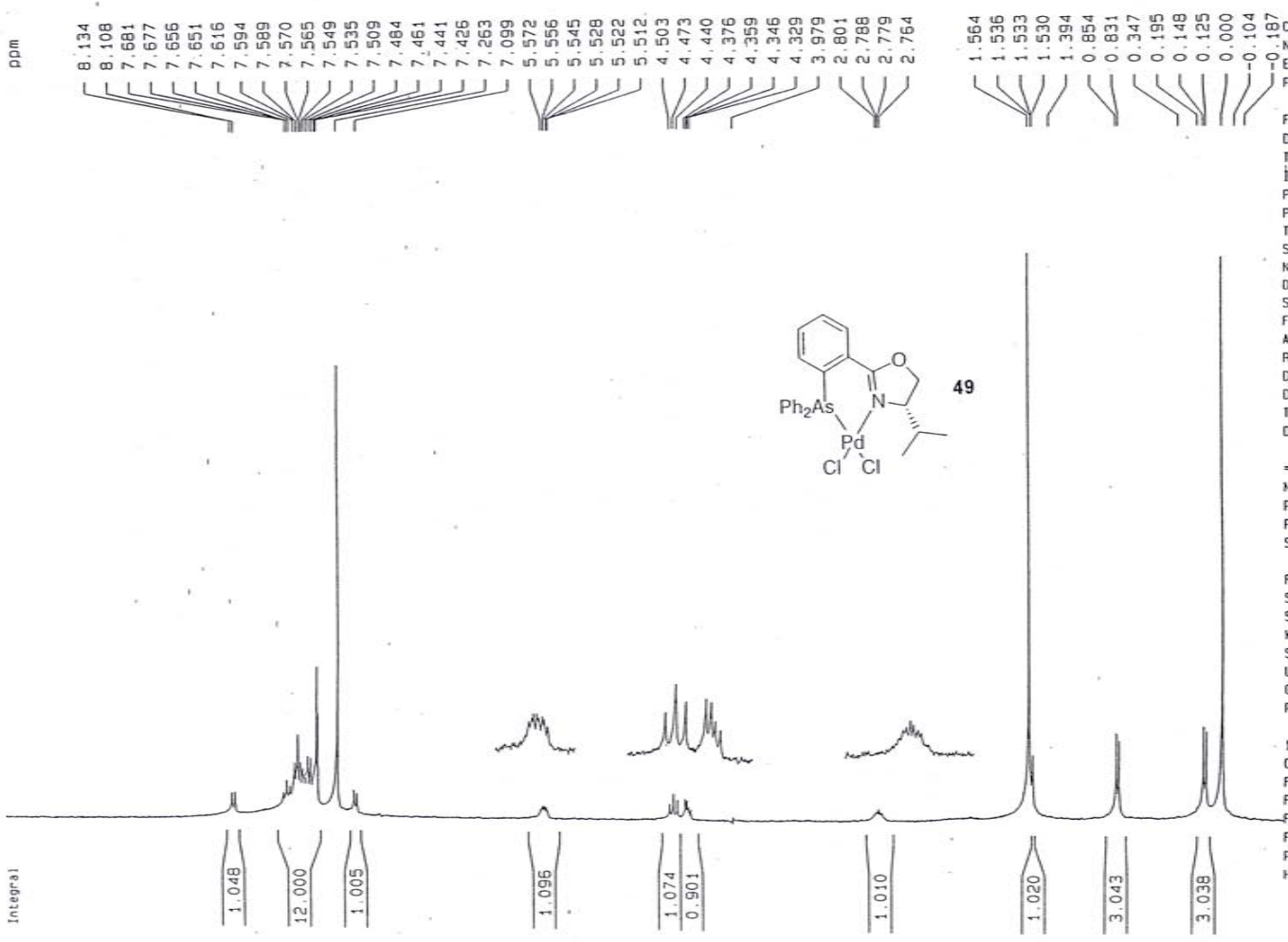
F2 - Processing parameters

SI	32768
SF	300.1300095 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm

MY 163



Current Data Parameters
NAME my163
EXPNO 1
PROCNO 1

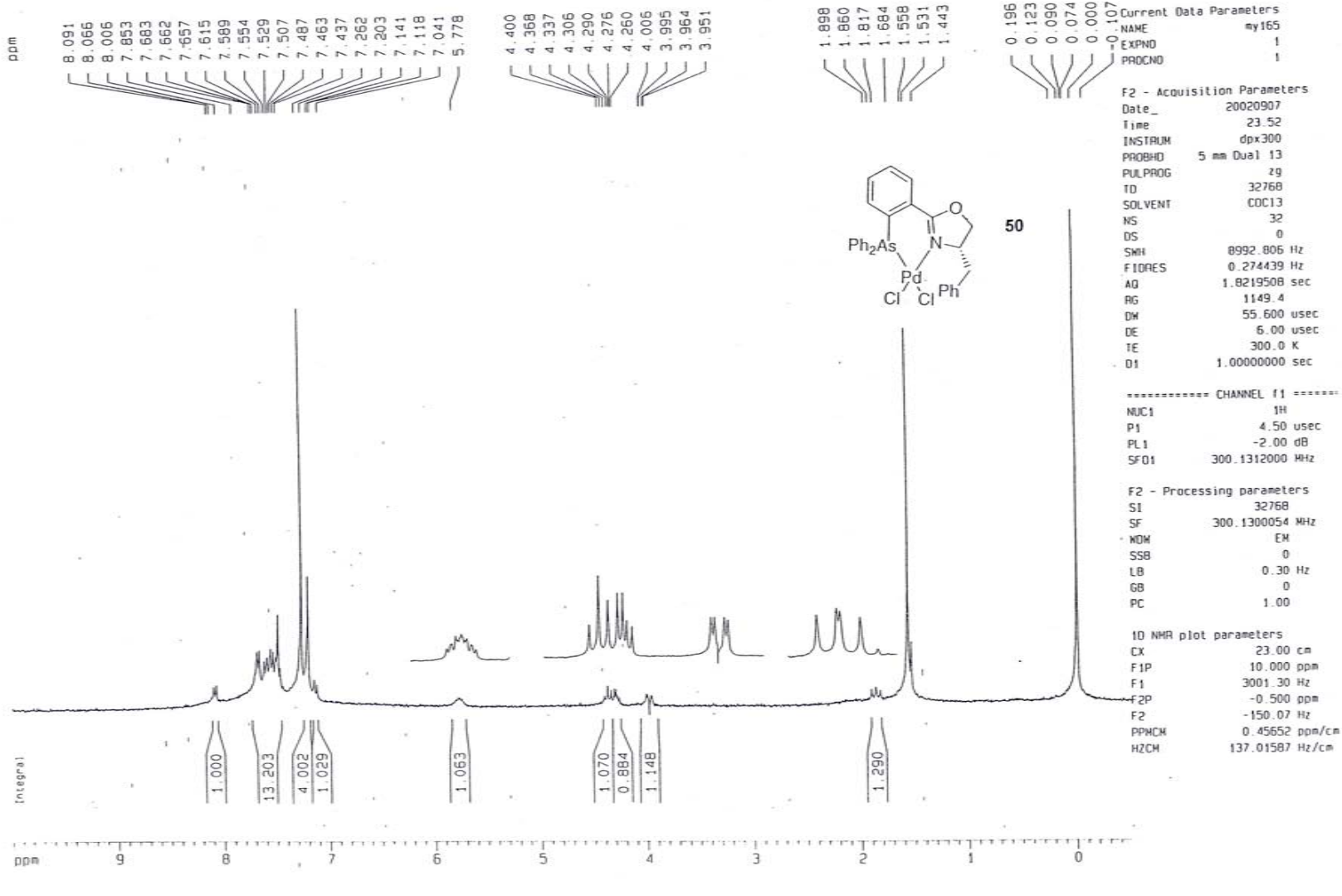
F2 - Acquisition Parameters
Date_ 20020907
Time 23.30
INSTRUM dpx300
PROBHD 5 mm Dual 13
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 1290.2
DW 55.600 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

========== CHANNEL f1 =======
NUC1 1H
P1 4.50 usec
PL1 -2.00 dB
SFO1 300.1312000 MHz

F2 - Processing parameters
SI 32768
SF 300.1300054 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 23.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.45652 ppm/cm
HZCM 137.01587 Hz/cm

MY 165



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Current Data Parameters

NAME	my165
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20020907
Time	23.52
INSTRUM	dpx300
PROBHD	5 mm Dual 13
PULPROG	zg
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	8992.806 Hz
FIDRES	0.274439 Hz
AQ	1.8219508 sec
RG	1149.4
DW	55.600 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 =======

NUC1	1H
P1	4.50 usec
PL1	-2.00 dB
SFO1	300.1312000 MHz

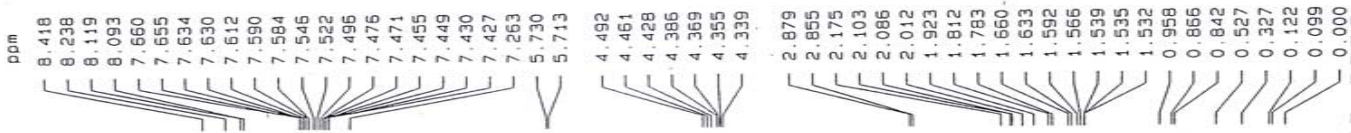
F2 - Processing parameters

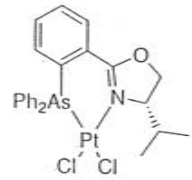
SI	32768
SF	300.1300054 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

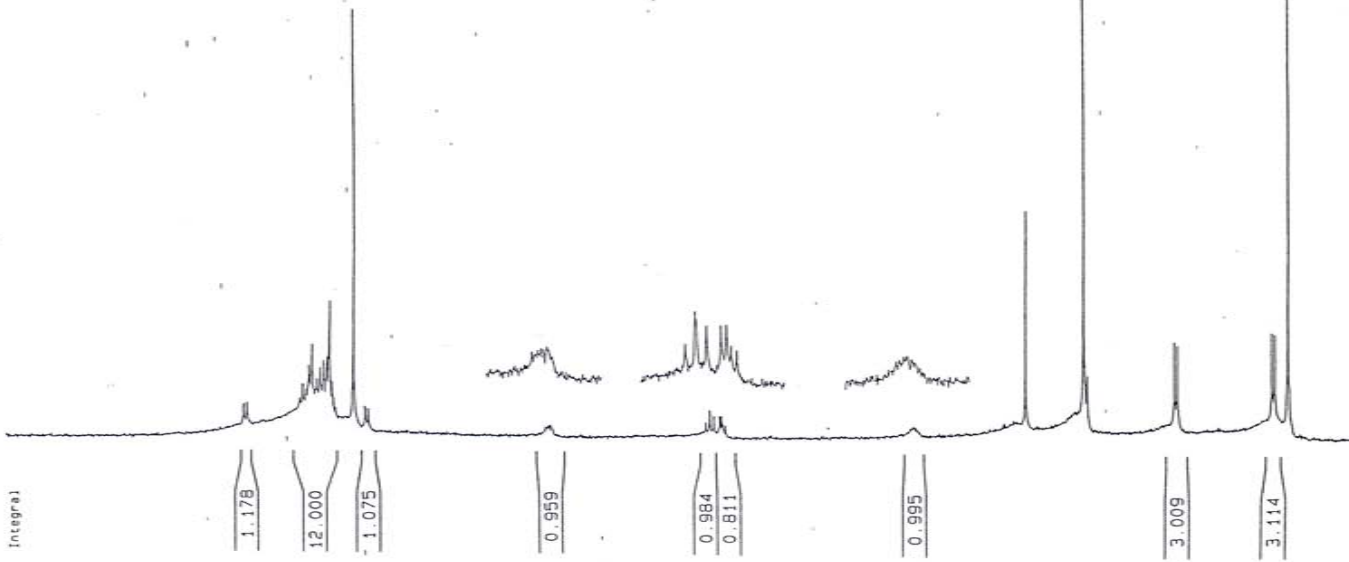
CX	23.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45652 ppm/cm
HZCM	137.01587 Hz/cm

my177





51



Current Data Parameters
NAME my177
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020925
Time 18.35
INSTRUM dpx300
PROBHD 5 mm Dual 13
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 1625.5
DW 55.600 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

========== CHANNEL f1 ========
NUC1 1H
P1 4.50 usec
PL1 -2.00 dB
SFO1 300.1312000 MHz

F2 - Processing parameters
SI 32768
SF 300.1300054 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 23.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.45652 ppm/cm
HZCM 137.01587 Hz/cm